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Chemistry I

Course and exercises



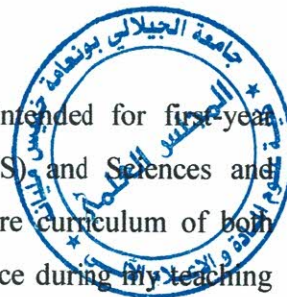
1st year bachelor's degree in matter sciences

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PREFACE

This course on "Chemistry 1" (Structure of Matter) is intended for first-year university students in the fields of Matter Sciences (MS) and Sciences and Technology (ST). It aligns with the first-year common core curriculum of both disciplines. This is a personal work stemming from my own experience during my teaching activities in the matter structure module.



It is designed to provide a set of fundamental knowledge on the laws and concepts necessary for understanding the structure of matter. This subject aims to equip students with the basic formalisms of chemistry, particularly in areas describing the atom and chemical bonding, chemical elements and the periodic table, along with energy quantification.

The adopted structure offers a progressive approach to general chemistry. This course is divided into four chapters:

- The first chapter of this course primarily focuses on the fundamental concepts of general chemistry, including a review of matter, atoms, and molecules. It is dedicated to the classical conception of the atom and will cover generalities about atomic structure, as well as the various experiments that revealed its constituents, protons, neutrons, the nucleus, and electrons. It also addresses radioactivity and nuclear reactions.
- Chapter 2 deals with energy quantification in the atomic model (wave-particle duality of light, the hydrogen spectrum, and classical atomic models) and the study of the wave model of the atom.
- Chapter 3 is devoted to the periodic classification of elements, and the evolution and periodicity of the physicochemical properties of elements.
- The fourth and final chapter covers chemical bonding: ionic bonding, covalent bonding, Lewis structures, the VSEPR method, and the hybridization of atomic orbitals.

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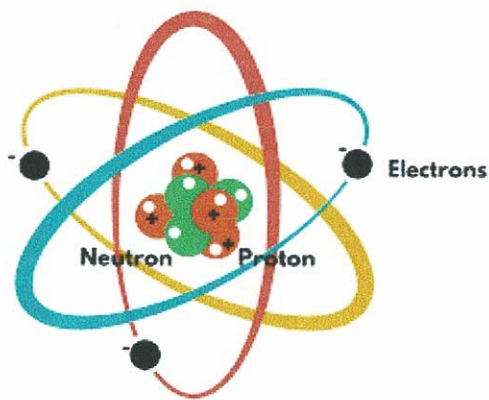
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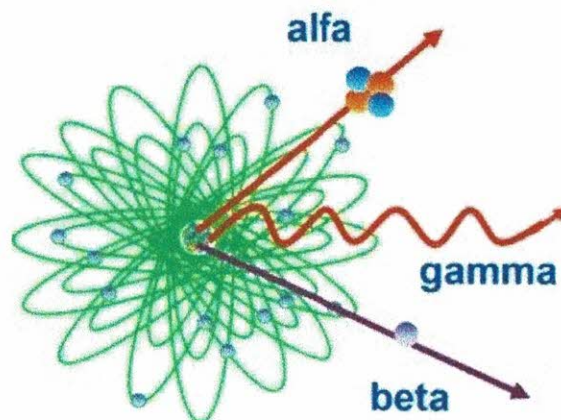
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Chapter 1 *Atomic Structure*



Chapter 1

Atomic Structure

1.1. Fundamental Concepts

1.1.1. Definition of Matter

Matter is anything that occupies space and has mass. All matter, at least in principle, can exist in three states: solid, liquid, and gas (Fig 1.1):

- **Solids** have definite shapes and definite volumes. They are incompressible.
- **Liquids** have a definite volume but no specific shape; they take the shape of their container. They are slightly compressible.
- **Gases** have neither a definite volume nor shape; they take the volume and shape of their container. They are highly compressible.

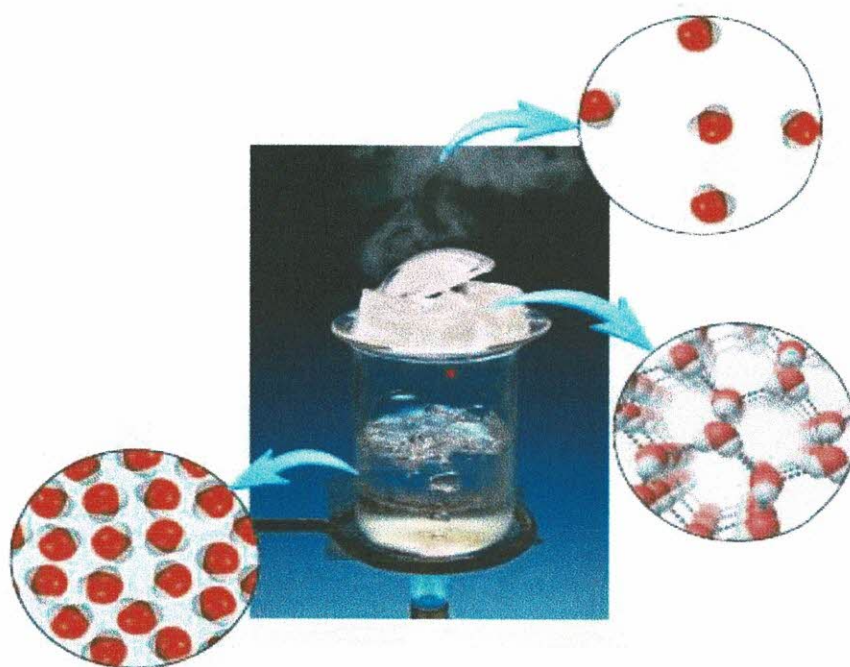


Figure 1.1: The three states of matter for water: solid ice, liquid water, and gaseous steam.

1.1.2. Changes in states of matter

The transition from one state of matter to another is called a change of state. This change is brought about by a change in volume, temperature and/or pressure. There are two types of change: **physical change** and **chemical change**.

1.1.2.1. Physical Change

A physical change is a transformation that does not alter the nature of a substance; it simply involves a change in its state, shape, or physical dimensions. The transition between states is illustrated in the diagram below (Fig. 1.2):

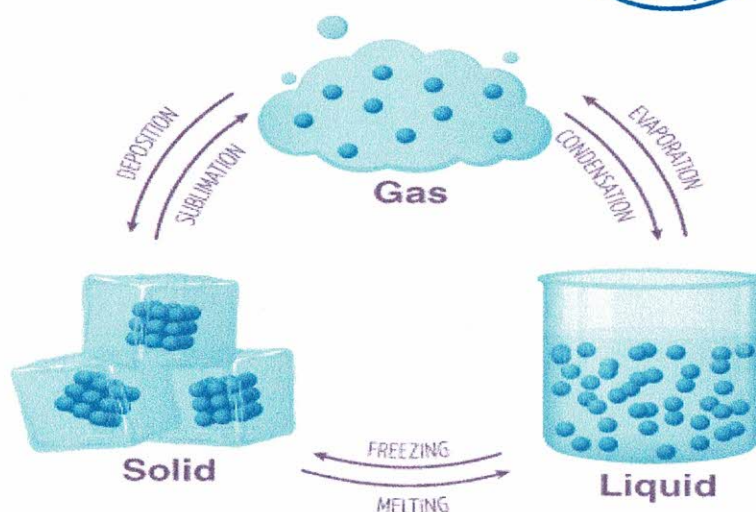


Figure 1.2: Changes of state of matter.

Examples: evaporation of water, dissolving of sugar.

1.1.2.2. Chemical change

In a chemical change, or chemical reaction, one or more kinds of matter are converted to new kinds of matter with different compositions.

Examples: conversion of iron to rust, conversion of gasoline to carbon dioxide and carbon monoxide.

1.1.3. Classification of Matter

Matter is made up of very tiny units called atoms, which serve as the fundamental components of chemical elements. According to the International Union of Pure and Applied Chemistry (IUPAC), there are currently 118 recognized elements. These range from abundant examples like carbon, iron, and silver to more obscure ones, such as lutetium and thulium. Approximately 90 of these elements are found in nature, while the rest are synthetically produced in laboratory settings.

Matter can be classified into two fundamental categories: **pure substances** and **mixtures**. The flow diagram in Fig. 1.3 is a pictorial representation of this.

1.1.3.1. Pure Substances

A pure substance has a definite and constant composition and distinct chemical properties. It is the same throughout. Pure substances are either elements or compounds:

a. Elements: Cannot be broken down into simpler substances by chemical means. They consist of only one type of atom.

Examples: Gold (Au), Oxygen (O), Aluminum (Al), Helium (He).

b. Compounds: Consist of two or more different elements chemically bonded together in a fixed proportion. They can be broken down into elements by chemical means.

Examples: Water (H₂O), Sodium Chloride (NaCl), Carbon Dioxide (CO₂).

1.1.3.2. Mixtures

A mixture consists of two or more different substances that are physically combined (not chemically bonded). The composition of a mixture is variable. They are divided into two categories:

a. Homogeneous Mixtures (solutions): Have a uniform composition throughout. The different components are not visually distinguishable.

Examples: Air, Saltwater, Brass (an alloy), Sweet tea.

b. Heterogeneous Mixtures: Do not have a uniform composition. The components remain distinct and are often visually distinguishable.

Examples: Salad, Granite, Oil and vinegar, Chocolate chip cookies.

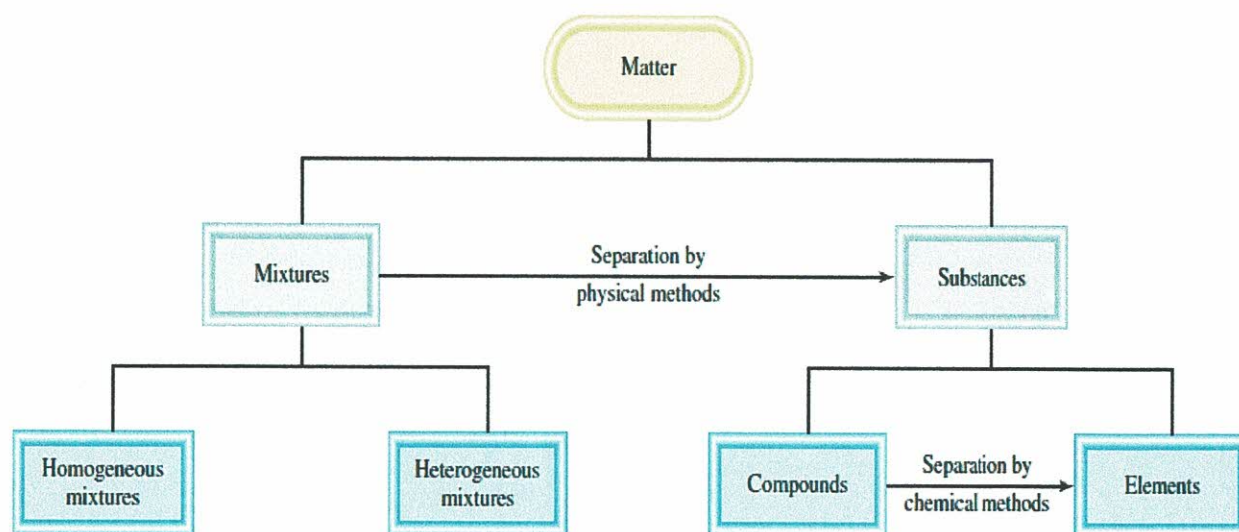


Figure 1.3: Classification of matter.

1.1.4. Concept of atom, molecules, mole and Avogadro's number

1.1.4.1. Atom: An atom is the smallest unit of ordinary matter that forms a chemical element.

The size of an atom is very small in angstroms ($1\text{\AA} = 10^{-10}\text{ m}$) and its mass is about 10^{-26} kg

- ✓ **Ion:** An atom that has gained or lost electrons, giving it a net positive or negative charge.
- ✓ An **anion** is a negatively charged ion.
- ✓ A **cation** is a positively charged ion.

1.1.4.2. Molecule: A molecule is a group of two or more atoms held together by the forces of chemical bonds.

1.1.4.3. Mole: The mole (mol) is the SI unit for amount of substance. It is defined as the amount of any substance that contains exactly $6.02214076 \times 10^{23}$ elementary entities (e.g., atoms, molecules, ions, electrons).

1.1.4.4. Avogadro's number: Avogadro's number (N_A) is the number of constituent particles (usually atoms or molecules) in one mole of a given substance.

$$N_A = 6,02214076 \times 10^{23} \text{ mol}^{-1}$$

1 mole of atoms, ions, molecules... = $6,02214076 \times 10^{23}$ atoms, ions, molecules....

1 mole of iron (Fe) atoms = $6,022 \times 10^{23}$ iron atoms.

1 mole of water (H_2O) molecules = $6,022 \times 10^{23}$ water molecules.

1 mole of sodium ions (Na^+) = $6,022 \times 10^{23}$ sodium ions.

1.1.4.5. Atomic molar mass: The molar mass of an element is the mass of one mole of atoms of that element, measured in grams per mole (g/mol), and is denoted by the letter M.

Example:

Molar mass of carbon = 12,01 g/mol (for one mole of carbon atoms); $M_C = 12,01 \text{ g/mol}$.

1.1.4.6. Molecular molar mass: or mass of a chemical substance is the mass of one mole of a molecule of that substance. It is determined by taking the sum of all the atomic molar masses of all the chemical elements present in the molecule.

Example

- The molecular mass of H_2O is: $M_{\text{H}_2\text{O}} = 2 M(\text{H}) + M(\text{O})$

$$M(\text{H}_2\text{O}) = 2 \times 1,01 + 16 = 18,02 \text{ g/mol.}$$

- The molecular mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is: $M_{\text{C}_6\text{H}_{12}\text{O}_6} = 6 M(\text{C}) + 12 M(\text{O}) + 12 M(\text{H})$

$$M_{\text{C}_6\text{H}_{12}\text{O}_6} = 6 \times 12,01 + 12 \times 1,01 + 6 \times 16,00 = 180,18 \text{ g/mol}$$

1.1.4.7. Atomic mass unit (amu): The amu is defined as one-twelfth the mass of a particular kind of atom of the element carbon, the so-called **carbon-12 atom**.

$$1 \text{ amu} = (1/12) \times (\text{the mass of an atom of } {}^6_{12}\text{C})$$

Calculation of the mass of an atom of ${}^6_{12}\text{C}$

$$\begin{array}{lcl} 1 \text{ mole of atoms } {}^6_{12}\text{C} & \longrightarrow & N_A \text{ atoms } {}^6_{12}\text{C} \longrightarrow 12\text{g} \\ & & 1 \text{ atom of } {}^6_{12}\text{C} \longrightarrow m_{\text{atom}} \end{array} \left. \vphantom{\begin{array}{lcl} 1 \text{ mole of atoms } {}^6_{12}\text{C} \\ & & 1 \text{ atom of } {}^6_{12}\text{C} \end{array}} \right\} \text{Therefore: } m_{\text{atom}} = 12/N_A$$

$$1 \text{ amu} = (1/12) \times (12/N_A) = 1/N_A = 1/6,02214076 \times 10^{23} \text{ (g)}$$

$$1 \text{ u.m.a} = 1,660539067 \times 10^{-24} \text{ g} = 1,660539067 \times 10^{-27} \text{ Kg}$$

1.1.4.8. Molar volume: The molar volume (V_m) is the volume occupied by one mole of a substance in the gaseous state and under Standard Temperature and Pressure (STP).

Temperature = 0 °C (273.15 K)

Pressure = 1 atm (101,325 kPa)

$$V_m = \frac{V}{n} [\text{m}^3/\text{mol or L/mol}]$$

One mole of gas occupies a volume of 22,414 liters, $V_m = 22.414 \text{ L/mol}$.

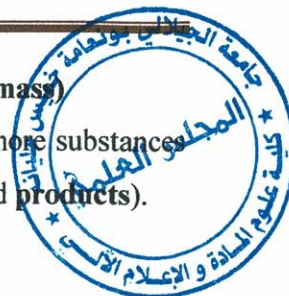
1.1.5. The components of a solution

Solution: A solution is a homogeneous mixture composed of two or more substances. The components are:

- ✓ **Solute:** The substance being dissolved (lesser amount).
- ✓ **Solvent:** The substance doing the dissolving (greater amount).

Note: A solution with water as the solvent is called an aqueous solution.

- ✓ **Dilute solution:** A dilute solution is one that has a relatively small amount of dissolved solute compared to the amount of solvent.
- ✓ **Saturated solution:** A saturated solution is one that has reached its maximum capacity to dissolve a solute at a given temperature.

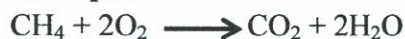


1.1.6. Chemical reaction and Lavoisier's law (The Law of conservation of mass)

1.1.6.1. Chemical reaction: A chemical reaction is a process where one or more substances (called **reactants**) are transformed into one or more different substances (called **products**).



Example:



1.1.6.2. Lavoisier's law

In a closed system, **mass is neither created nor destroyed** in a chemical reaction. The total mass of the reactants (starting materials) must equal the total mass of the products (resulting materials).

1.1.7. Quantitative aspect of matter

1.1.7.1. Number of moles (Amount of substance)

- From mass (in grams)

n : amount of substance in moles is the quotient of the mass of the substance and its molar mass

$$n \text{ (mol)} = m \text{ (g)} / M \text{ (g/mol)}$$

Example: How many moles are in 25 grams of water (H_2O)?

Molar mass of H_2O = 18,02 g/mol

$$n = m / M = 25 / 18,02 \approx 1,39 \text{ moles}$$

- From number of particles (Atoms, Molecules, etc.)

$$n \text{ (mol)} = N / N_A$$

n : number of moles (mol)

N : number of particles (e.g., atoms, molecules)

N_A : Avogadro's constant = $6,022 \times 10^{23}$ particles/mol

Example: A sample contains $3,011 \times 10^{24}$ molecules of CO_2 . How many moles is this?

$$n = N / N_A = (3,011 \times 10^{24}) / (6,022 \times 10^{23}) = 5,000 \text{ moles}$$

- From volume of a gas (at Standard Temperature and Pressure - STP)

$$n \text{ (mol)} = V \text{ (L)} / V_m \text{ (L/mol)}$$

V: volume of the gas (L)

V_m : molar volume = 22,4 L/mol (at STP)

Example: What is the number of moles in 67,2 liters of oxygen gas (O_2) at STP?

$$n = V / V_m = 67,2 / 22,4 = 3.00 \text{ moles}$$

- **From concentration (for solutions)**

$$n \text{ (mol)} = C \text{ (mol/L)} \times V \text{ (L)}$$

C: concentration (molarity, mol/L or M)

V: volume of solution (L)

Example: How many moles of NaCl are in 0,5 liters of a 2,0 M (or mol/L) NaCl solution?

$$n = C \times V = 2,0 \times 0,5 = 1,0 \text{ mole}$$

1.1.7.2. Molar concentration (Molarity):

Molar concentration (also called molarity) is a measure of the concentration of a chemical species in a solution. It is defined as the number of moles of a solute divided by the volume of the solution.

$$C \text{ (mol/L)} = n \text{ (mol)} / V \text{ (solution) (L)}$$

Example: A student prepares a solution by dissolving 29,25 grams of sodium chloride (NaCl) in enough water to make a final solution volume of 500 mL.

1. Calculate the number of moles of NaCl in the solution.
2. What is the molar concentration (molarity) of the solution?

The number of moles of NaCl = $n = \text{mass} / \text{molar mass}$.

$$\text{Molar mass of NaCl} = 23 + 35,45 = 58,45 \text{ g/mol}$$

$$n = 29,25 / 58,5 = 0,5 \text{ moles}$$

$$\text{Molarity} = C = n / V = 0,5 / 0,5 = 1 \text{ mol/L.}$$

1.1.7.3. Mass concentration

Is the ratio of the mass of solute present per liter of solution. Mass concentration is denoted by C_m and is expressed in g/L.

$$C_m \text{ (g/L)} = m \text{ (g)} / V_{\text{solution}} \text{ (L)}$$

Example

1. A solution with a volume of $V = 250 \text{ mL}$ is prepared by dissolving $0,012 \text{ mol}$ of sucrose in water. What is the molar concentration of sucrose in mol/L ?
2. A runner prepares $V = 1,0 \text{ L}$ of sugar water by placing 6 sugar cubes in a jug and filling it to the brim with water. Each sugar cube (sucrose with the chemical formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) has a mass of $5,6 \text{ g}$.

a- Calculate the mass concentration of sucrose in the sugar drink.

b- Determine the molar concentration C of the solution.

1. $C = n / V$, $V = 250 \text{ ml} = 0,25 \text{ L}$, $C = 0,012 / 0,25 = 4,8 \times 10^{-2} \text{ mol/L}$.

2. a- $V = 1,0 \text{ L}$, mass of 6 sugar cubes $= 6 \times m(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 6 \times 5,6 = 33,6 \text{ g}$

$C_m = m(\text{solute}) / V(\text{solution})$. $C_m = 33,6 / 1 = 33,6 \text{ g/L}$.

$C = n(\text{solute}) / V(\text{solution})$. $n = m/M = 33,6 / 342 = 0,098 \text{ mol} = 9,8 \times 10^{-2} \text{ mol}$

$C = 0,098 / 1 = 0,098 \text{ mol/L}$.

1.1.7.4. Molal concentration (Molality)

The number of moles of solute dissolved in one kilogram of solvent.

$$m_{\text{mol}} (\text{mol/kg}) = n (\text{mol}) / m_{\text{solvent}} (\text{kg})$$

Example

Calculate the molality of a solution prepared by dissolving 25 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in 500 g of water.

Moles of glucose:

$$n = m/M = 25/180 = 0,139 \text{ mol}$$

Apply the molality formula: $m_{\text{mol}} = 0,139/0,5 = 0,278 \text{ mol/kg}$.

1.1.7.5. Normality

Is the number of grams equivalent of an element dissolved in one liter of solution. The units of concentration are denoted by the symbols N , eq/L .

$$N (\text{eq-g/L}) = n (\text{g-eq}) / V_{\text{solution}} (\text{L})$$

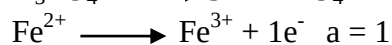
Number of gram equivalent = Mass of solute/Equivalent weight

Equivalent weight = Molecular weight of solute / a (a = valence factor, where valence factor for acids and bases is the number of H^+ and OH^- ions they release in the solution, respectively).

The following simple relationship exists between normality, N , and molarity, C .

$$N = a \times C$$

Example



1.1.7.6. Molar fraction

$$x_i = n_i / \sum n_i$$

- The molar fraction is unitless.
- The sum of the molar fractions of all components of the solution is always equal to 1. $\sum x_i = 1$
- The molar percentage is the molar fraction multiplied by 100%.

1.1.7.7. Mass fraction

$$w_i = m_i / \sum m_i$$

- The mass fraction is unitless.
- The sum of the mass fractions of all components of the solution is always equal to 1. $\sum w_i = 1$
- The mass percentage is the mass fraction multiplied by 100%.

1.1.7.8. Density

It expresses the mass of a certain volume of solution under specific temperature and pressure conditions. It is denoted as ρ and its unit is g/L.

$$\rho \text{ (g/L)} = \text{mass of the solution} / \text{volume of the solution}$$

1.1.7.9. Relative density or specific gravity

a. For liquids relative to water

The relative density of a liquid or solid is the ratio of the density of that liquid or solid to the density of water.

$$d = \rho / \rho_{\text{water}}$$

b. For gases

The relative density of a gas relative to air is the quotient of the mass m of a volume v of gas to the mass m_{air} of the same volume of air (reference substance), where m and m_{air} are measured under the same temperature and pressure conditions.

$$d = \rho_{\text{gas}} / \rho_{\text{air}} = \rho_{\text{gas}} \times V / \rho_{\text{air}} \times V = m_{\text{gas}} / m_{\text{air}}$$

If the volume considered is the molar volume, then $m = M$ (molar mass), knowing that the density of dry air is 1,293 g/L

$$m_{\text{air}} = \rho_{\text{air}} \times V_{\text{mol}} = 1,293 \times 22,4 = 29 \text{ g}$$

Therefore:

$$d = M/29$$

Note: Relative density has no unit.

Exercise

The density of an aqueous solution of sodium hydroxide is 1,43. This solution contains 40% by weight of NaOH.

1. What is the mass of one liter of solution?
2. What is the mass of NaOH in one liter of solution?
3. What is the molarity of the solution?
4. What is the mass of NaOH per kilogram of water?
5. What is the molality of the solution?

Correction

1. Calculation of the mass of solution:

We have: $d = \rho_{\text{solution}} / \rho_{\text{water}} = \rho_{\text{solution}}$

$$d = \rho = m/V \rightarrow m = d \times V = 1,43 \times 10^3 = 1430 \text{ g} = 1,43 \text{ Kg}$$

2. Calculation of the mass of NaOH in 1L of solution:

$$\% \text{ mass of NaOH} = (m_{\text{NaOH}} / m_{\text{solution}}) 100$$

$$m_{\text{NaOH}} = 40 \times 1430 / 100 \rightarrow m_{\text{NaOH}} = 572 \text{ g}$$

3. Calculation of molarity:

$$C = n_{\text{NaOH}} / V = (m_{\text{NaOH}} / M_{\text{NaOH}}) \times V = 572 / 40.1 = 14,3 \text{ mol/L}$$

4. Calculation of m_{NaOH} in 1 kg of water:

1L of solution weighs 1430 g including 572 g of NaOH and 858 g of water.

So :

$$\left. \begin{array}{l} 572 \text{ g of NaOH} \longrightarrow 858 \text{ g of H}_2\text{O} \\ m_{\text{NaOH}} \longrightarrow 1000 \text{ of H}_2\text{O} \end{array} \right\}$$
$$m_{\text{NaOH}} = 572 \times 1000 / 858 = 666,66 \text{ g}$$

5. Calculation of the molality of the solution:

$$m_{\text{mol}} = n_{\text{NaOH}} / m_{\text{solvant}}$$

$$n_{\text{NaOH}} = m / M = 666,66 / 40 = 16,66 \text{ moles}$$

$$m_{\text{mol}} = 16,66/1 = 16,66 \text{ mol/Kg}$$

1.2. The Structure of the Atom

On the basis of Dalton's atomic theory, we can define an **atom** as the basic unit of an element that can enter into chemical combination. Dalton imagined an atom that was both extremely small and indivisible. However, a series of investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms actually possess internal structure; that is, they are made up of even smaller particles, which are called subatomic particles. This research led to the discovery of three such particles: electrons, protons, and neutrons.

1.2.1. Discovery of the electron

1.2.1.1. Electrical Nature of Matter

One of the most significant early indications in discovering the electrical nature of matter and the relationship between matter and electricity emerged from the experimental research conducted by scientist Faraday in 1833 in the field of electrochemical analysis (**Fig. 1.4**).

When passing an electric current through this solution consisting of dissolved copper sulfate in water:

- Positive ions (Cu^{2+}) move towards the negative electrode.
- Negative ions (SO_4^{2-}) move towards the positive electrode.

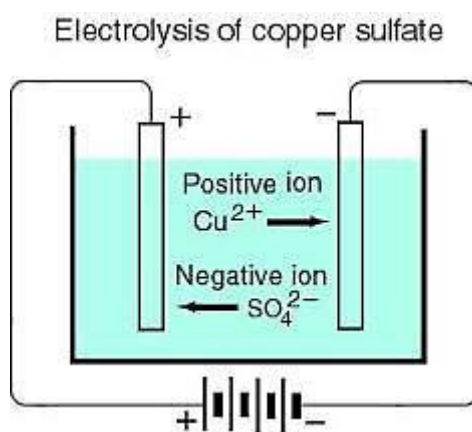


Figure 1.4: Faraday's experiment.

It has been found that the weight of the substance deposited on one of the electrodes is proportional to the amount of electricity passing through the solution.

- If we represent q as the amount of electricity associated with the appearance of a copper atom at the negative electrode. Therefore, $2q, 3q, \dots, nq$ represents the amount of electricity resulting from the deposition of 2, 3, ..., n copper atoms at the cathode.
- The emergence of these whole number quantities of electricity led scientists to assume that electricity is composed of elementary charges, and that atoms contain such charges.

1.2.1.2. Proof of the existence of the electron

- The physicist **William Crookes (1879)** considered, with the help of his discharge tube, that cathode rays are composed of negative particles.
- In 1891, **Stoney** named the particles constituting cathode rays as electrons.
- **Joseph John Thomson's** experiment in 1895 enabled the calculation of the ratio e/m_e .

$$e/m_e = 1,759 \times 10^{11} \text{ Coulombs/Kg}$$

- In 1911, **Robert Millikan** was able to determine the value of the electron's charge by studying the movements of an electrified oil droplet between the plates of a horizontal capacitor.

$|e|$ is identified with the absolute value of the electron's charge, which is negative:

$$|e| = 1,60217733 \times 10^{-19} \text{ C (coulombs)}$$

the ratio $|e|/m$ and the elementary charge $|e|$, it is easy to deduce the mass of the electron.

$$|e|/m = 1,759.10^{11} \text{ C. Kg}^{-1} = A$$

$$|e| = 1,60217733 \cdot 10^{-19} \text{ C}; \text{ therefore : } m = A/|e| = 1,759.10^{11} / 1,60217733.10^{-19}$$

$$m_e = 9,109\,3897 \times 10^{-31} \text{ Kg} = 0,00055 \text{ amu}$$

1.2.2. The Nucleus discovery

Goldstein (1886) repeated the experiment with a discharge tube filled with a perforated cathode and found that new type of rays came out through the hole in the cathode. When this experiment is conducted, a faint red glow is observed on the wall behind the cathode (**Fig. 1.5**). Since these rays originate from the anode, they are called anode rays (canal rays). They are composed of positively charged particles.

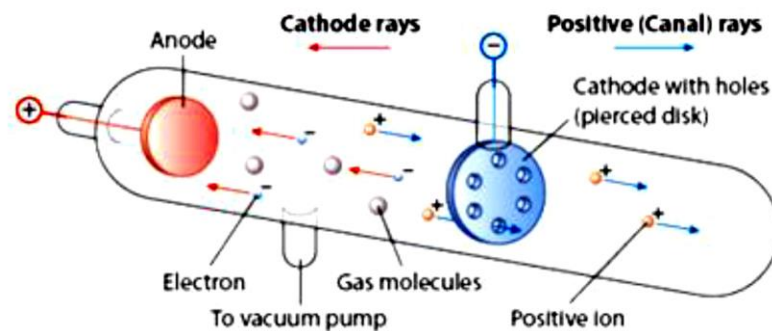


Figure 1.5 : Goldstein's experiment

1.2.2.1. Nucleus components:

a. Proton

The proton was discovered by Rutherford by bombarding nitrogen atoms with particles (α) according to the following nuclear reaction:



Protons are positively charged.

$$q_p = +e = 1,60217733 \times 10^{-19} \approx 1,602 \times 10^{-19} \text{ C}$$

The mass of a proton is 1836 times that of an electron

$$m_p = 1836 m_e = 1,672623 \cdot 10^{-27} \text{ Kg} = 1,007276470 \text{ amu}$$

b. Neutron (Chadwick Experiment (1932))

Chadwick bombarded beryllium with alpha particles (He nuclei) and observed the production of neutral radiation that was not affected by magnetic or electric fields (Fig. 1.6). These radiations consisted of neutral particles, which were called neutrons with a mass approximately equal to the proton.



$$m_n = 1838 m_e = 1,67493 \cdot 10^{-27} \text{ Kg} = 1,00866 \text{ amu}$$

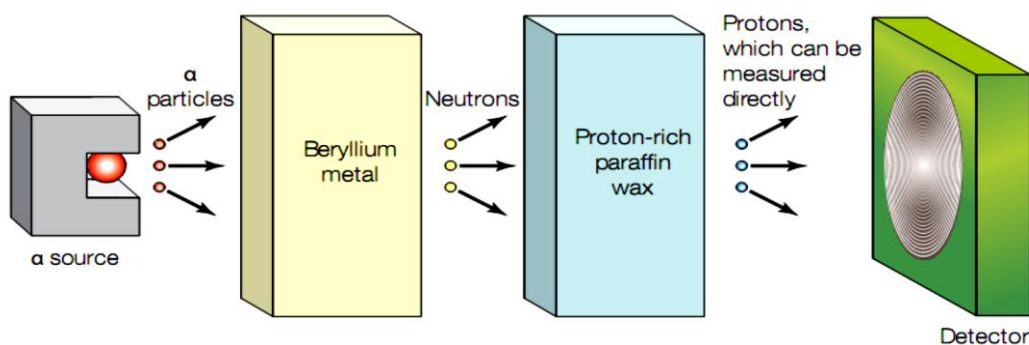


Figure 1.6: Chadwick's experiment.

The properties of the subatomic particles are summarized in the following table:

Table 1.1: The properties of the subatomic particles

Particle	Mass (g)	Mass (amu)	Charge (C)	Charge (e)
Electron	$9,10938 \times 10^{-28}$	0,00055	$-1,60218 \times 10^{-19}$	- 1
Proton	$1,67262 \times 10^{-24}$	1,00727	$+1,60218 \times 10^{-19}$	+ 1
Neutron	$1,67493 \times 10^{-24}$	1,00866	0	0

1.2.3. The Nuclear Model of the Atom

1.2.3.1. Thomson's Model of the atom

Thomson proposed that an atom could be thought of as a uniform, positive sphere of matter in which electrons are embedded (**Fig. 1.7**). Thomson's so-called "plum pudding" model was the accepted theory for a number of years.

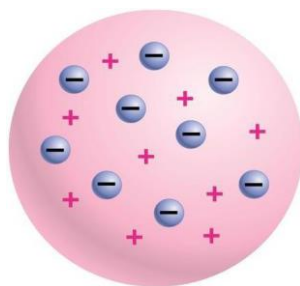


Figure 1.7: Thomson's atomic model.

1.2.3.2. Rutherford's model of the atom

Rutherford's experiment: Rutherford conducted a series of experiments using α -particles. A beam of α -particles was directed against a thin foil of gold, platinum, silver, or copper. The foil was surrounded by a circular fluorescent zinc screen. Whenever an α -particle struck the screen, it produced a flash of light (**Fig. 1.8**).

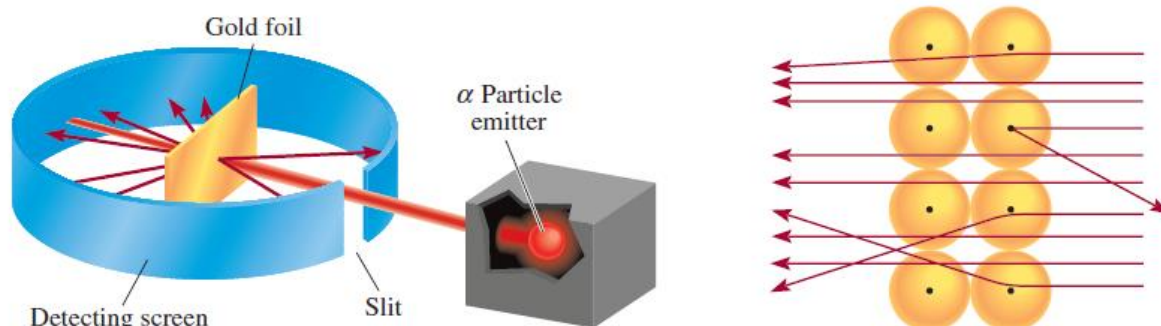


Figure 1.8: Rutherford's experiment.

- ❖ Most of the α particles passed straight through the gold foil without being deflected, indicating that there must be very large empty space within the atom.
- ❖ A few of them were deflected through small angles, while a very few were deflected to a large extent, indicating that whole of the positive charge is concentrated in a space called nucleus. It is proposed to be present at the center of the atom.
- ❖ A very small percentage (1 in 10000) was deflected through angles ranging from nearly 180° , indicating that the nucleus is rigid and α -particles recoil due to direct collision with the positively charged heavy mass.

The **Rutherford model**, also known as the **planetary model** or the nuclear model (**Fig. 1.9**), was a revolutionary step in understanding atomic structure, proposed by Ernest Rutherford in 1911 based on his famous gold foil experiment. Here are the key features, postulates, and significance of the Rutherford atomic model.

Rutherford's model was a radical departure from the previous "plum pudding" model. Its core ideas were:

- ❖ Most of the mass and all of the positive charge of an atom are centered in a very small region called the *nucleus*. The remainder of the atom is mostly *empty space*.
- ❖ The magnitude of the positive charge is different for different atoms and is approximately one-half the atomic weight of the element.
- ❖ There are as many electrons outside the nucleus as there are units of positive charge on the nucleus. The atom as a whole is electrically neutral.

The volume of the nucleus is negligibly small as compared to the volume of the atom.

$$\frac{\text{Diameter of atom}}{\text{Diameter of the nucleus}} = \frac{r_a}{r_n} = \frac{10^{-10}}{10^{-14}} = 10^4$$

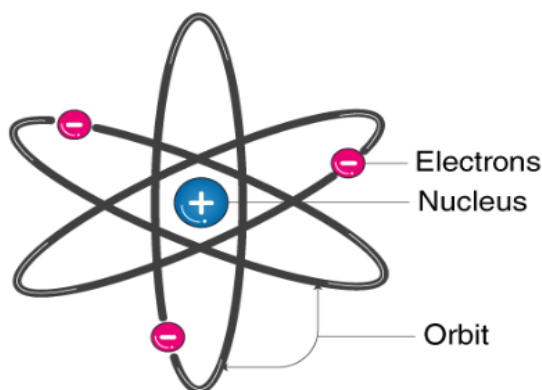


Figure 1.9: Rutherford's atomic model.

1.2.4. Presentation and characterization of the atom

All atoms can be identified by the number of protons (Z) and neutrons (N) they contain. A pair of these two values defines a nuclide. A nuclide 'X' is identified by the following symbolism (**Fig. 1.10**):

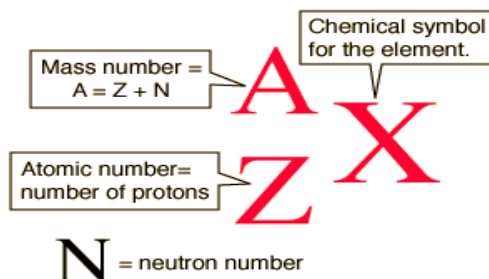


Figure 1.10 : Presentation of nucleus.

Z : is the number of protons, also known as the **atomic number**.

In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom.

A : is the number of nucleons, meaning the number of protons Z plus the number of neutrons N in the nucleus. Also known as the **mass number**.

$$\begin{aligned} \text{Mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{number of neutrons} \end{aligned}$$

The **neutron number**, is

$$N = A - Z$$

Example: The iron atom $^{56}_{26}\text{Fe}$ contains:

$Z = 26$ (26 protons in the nucleus therefore 26 electrons).

$A = 56$ (56 nucleons, so $N = 56 - 26 = 30$ neutrons in the nucleus).

- **Monoatomic ions**

Monoatomic ions are formed from the atom by the loss or gain of one or more electrons. During the transition from atom to ion, the nucleus is not altered (Z remains unchanged).

Example

- Copper ion $^{63}_{29}\text{Cu}^{2+}$ contains: $Z = 29$ (29 protons and $29 - 2 = 27$ electrons as it has lost 2 electrons) and $A = 63$ (63 nucleons, therefore $N = 63 - 29 = 34$ neutrons).
- The chloride ion $^{35}_{17}\text{Cl}^-$ contains : $Z = 17$ (17 protons and $17 + 1 = 18$ electrons as it has gained 1 electron) and $A = 35$ (35 nucleons, therefore $N = 35 - 17 = 18$ neutrons).

Exercise

Give the number of electrons, protons and neutrons for the following atoms and ions: $^{55}_{25}\text{Mn}$, $^{56}_{26}\text{Fe}$, $^{57}_{26}\text{Fe}$, $^{24}_{12}\text{Mg}^{+2}$, $^{52}_{24}\text{Cr}^{+6}$, $^{35}_{17}\text{Cl}^{-}$, $^{79}_{34}\text{Se}^{2-}$.

Atom/ion	$^{56}_{26}\text{Fe}$	$^{57}_{26}\text{Fe}$	$^{24}_{12}\text{Mg}^{2+}$	$^{52}_{24}\text{Cr}^{6+}$	$^{35}_{17}\text{Cl}^{-}$	$^{79}_{34}\text{Se}^{2-}$
Protons	26	26	12	24	17	34
Neutrons	30	31	12	28	18	45
Electrons	26	26	10	18	18	36

1.2.5. Isotopy and relative abundance of the different isotopes

1.2.5.1. Isotopes

Isotopes are atoms that have the same atomic number Z and different mass numbers A , hence different numbers of neutrons.

Examples

Isotopes of Hydrogen: ^1_1H , ^2_1H , ^3_1H .

Isotopes of Carbon: $^{12}_6\text{C}$, $^{13}_6\text{C}$, $^{14}_6\text{C}$.

Isotopes of Uranium: $^{234}_{92}\text{U}$, $^{235}_{92}\text{U}$, $^{238}_{92}\text{U}$.

- ❖ Isotopes have similar physical properties.
- ❖ Isotopes of the same element have identical chemical properties, as they have the same number of electrons.
- ❖ Isotopes have different atomic masses, because they have different numbers of neutrons.
- ❖ Isotopes can have very different nuclear properties. Some isotopes are stable, while others are radioactive (radioisotopes) and will decay over time, emitting radiation.

1.2.5.2. Relative Abundance

Relative abundance refers to the percentage or proportion of a specific isotope of an element that occurs naturally compared to all the isotopes of that element. It is usually expressed as a percentage (%). The sum of the relative abundances of all isotopes for a given element must equal 100%. This value is determined experimentally using instruments like a mass spectrometer.

Example: The element chlorine has two stable isotopes:

Chlorine 35 has a relative abundance of 75,76 %.

Chlorine 37 has a relative abundance of 24,24 %.

1.2.5.3. Average atomic mass

The average atomic mass of an element is the weighted average mass of all the naturally occurring isotopes of that element, measured in atomic mass units (amu). It reflects both the mass and the relative abundance of each isotope. The average atomic mass can be calculated using the formula:

$$\text{Average mass} = \frac{\sum m_i \times x_i}{100}$$

m_i : Mass of isotope i, $m_i \approx A_i$: mass number of isotope i.

x_i : Relative abundance of isotope i (%), $\sum x_i = 100\%$.

Example: Calculate the average atomic mass of Magnesium.

Isotope	$^{24}_{12}\text{Mg}$	$^{25}_{12}\text{Mg}$	$^{26}_{12}\text{Mg}$
x_i (%)	78,60	10,10	11,30
m_i (amu)	23,9850	24,9858	25,9826

$$\text{Average mass} = [(23,9850 \times 78,60) + (24,9858 \times 10,10) + (25,9826 \times 11,30)] / 100 = 24,312 \text{ amu}$$

- **Isobars**

Isobars are atoms of different chemical elements that have the same mass number but different atomic numbers

Example: $^{40}_{18}\text{Ar}$ and $^{40}_{20}\text{Ca}$, $^{14}_6\text{C}$ and $^{14}_7\text{N}$

- **Isotones**

Isotones are atoms of different chemical elements that have the same number of neutrons (N) but different atomic numbers (Z) and therefore different mass numbers (A).

Example: $^{13}_6\text{C}$ and $^{14}_7\text{N}$, $^{12}_5\text{B}$ and $^{13}_6\text{C}$.

1.2.6. Mass defect (Δm) and the binding energy (ΔE or BE):

Experimentally, the mass of the nucleus is not equal to the sum of the masses of the nucleons, that is to say that we have: $Z \times m_p + (A-Z) \times m_n > m_{\text{nucleus}}$

$[Z \times m_p + (A-Z) m_n]$: represents the mass of the nucleons

The formation of a nucleus always involves a loss of mass called the mass defect, denoted as (Δm).

1.2.6.1. Mass Defect (Δm)

The mass defect (Δm) is the difference between the sum of the masses of its individual protons and neutrons and its actual mass.

The formula for calculating defect mass (Δm) can be expressed as:

$$\Delta m = [Z \times m_p + (A - Z) \times m_n] - m_{\text{nucleus}}$$

Where: Δm : mass defect (amu);

m_p : mass of a proton (1,007277 amu);

m_n : mass of a neutron (1,008665 amu);

m_{nucleus} : mass of nuclide;

Z: atomic number (number of protons); and **A**: mass number (number of nucleons).

1.2.6.2. Mass–Energy Equivalence

This loss of mass spontaneously transforms into energy, which is called the binding or cohesion energy of the nucleus, and it is given by the Einstein relation that relates mass and energy:

$$\Delta E = \Delta m \times C^2$$

Where C: speed of light in vacuum = 3×10^8 m/s

1.2.6.3. Binding energy (ΔE)

Binding energy is the energy required to separate an atomic nucleus completely into its constituent protons and neutron, or, equivalently, the energy that would be liberated by combining individual protons and neutrons into a single nucleus.

Units of binding energy

The main units used are:

- ✓ **Joules**,
- ✓ **eV** ($1 \text{ eV} = 1,6 \times 10^{-19} \text{ J}$)
- ✓ **MeV** ($1 \text{ MeV} = 10^6 \text{ eV}$).

The electron volt is defined as the energy gained by an electron when it traverses a potential difference (ddp) of 1 volt ($\text{eV} = 1,6 \times 10^{-19} \text{ J}$, $1 \text{ V} = 1,6 \times 10^{-19} \text{ J}$).

Mass of the atomic mass unit in terms of energy

$$\Delta m = 1 \text{ uma} = 1,66 \times 10^{-27} \text{ Kg}$$

$$\Delta E = \Delta m \times C^2 = 1,66 \times 10^{-27} \times (3 \times 10^8)^2 = 1,494 \times 10^{-10} \text{ J} = 931,5 \text{ MeV}$$

$$\begin{aligned} \Delta E \text{ (Joules)} &= \Delta m \text{ (kg)} \times C^2 \text{ (m/s)}^2 \\ \Delta E \text{ (MeV)} &= \Delta m \text{ (amu)} \times 931,5 \end{aligned}$$

Exercise

The nucleus of the nitrogen atom N ($Z = 7$) is formed of 7 neutrons and 7 protons.

- 1) Calculate in amu the theoretical mass of this nucleus.
- 2) Calculate the mass defect of nitrogen.
- 3) Calculate the binding energy of this nucleus in J and in MeV.

$$m({}^1_0n) = 1.00867 \text{ amu}, \quad m({}^1_1p) = 1.00727 \text{ amu}, \quad m_N = 14.007515 \text{ amu}$$

1. Theoretical Mass of the Nucleus

$$m_{\text{theoretical}} = 7 \times m_p + 7 \times m_n = 7 \times (1.00727 + 1.00867) = 7 \times 2.01594 = 14.11158 \text{ amu}$$

2. Mass Defect

Δm = theoretical mass - actual nuclear mass

$$= m_{\text{The}} - m_{\text{act}} = 14.11158 - 14.007515 = 0.104065 \text{ amu.}$$

3. Binding energy

$$\Delta E = \Delta m \times C^2 = 0.104065 \times 1.66 \cdot 10^{-27} \times (3 \times 10^8)^2 = 1.5547311 \times 10^{-11} \text{ J}$$

$$\Delta E = 1.55 \times 10^{-11} / 1.6 \times 10^{-13} = 96.875 \text{ MeV}$$

$$\text{Or } \Delta E = \Delta m \times 931.5 = 0.104 \times 931.5 = 96.87 \text{ MeV}$$

1.2.6.4. The stability of the nucleus

a. Binding energy by nucleons

The Binding Energy per Nucleon is the average energy required to remove a single proton or neutron from an atomic nucleus. It is calculated by dividing the total binding energy of the nucleus by its total number of nucleons (protons + neutrons).

$$\frac{\Delta E}{A} = \frac{\Delta m \times 931.5}{A}$$

The binding energy per nucleon is a measure of the stability of an atomic nucleus. Nuclei with higher binding energies by nucleon are generally more stable, while those with lower binding energies per nucleon are less stable.

Examples: ${}^{56}\text{Fe}$ 8,79 MeV/nucleon.

${}^{238}\text{U}$ 7,57 MeV/nucleon.

Iron (${}^{56}\text{Fe}$) is more stable than uranium (${}^{238}\text{U}$).

b. Aston curve

The Aston curve below (**Fig. 1.11**) shows the variation of $\Delta E / A$ as a function of the nucleon number.

- The curve shows a maximum around $A = 60$.
- For $50 < A < 80$, the curve represents a peak, indicating the most stable nuclei.
- The ends of the curve correspond to the most unstable nuclei.

- Light nuclei can fuse to form more stable nuclei.
- Heavy nuclei can split to form more stable nuclei.

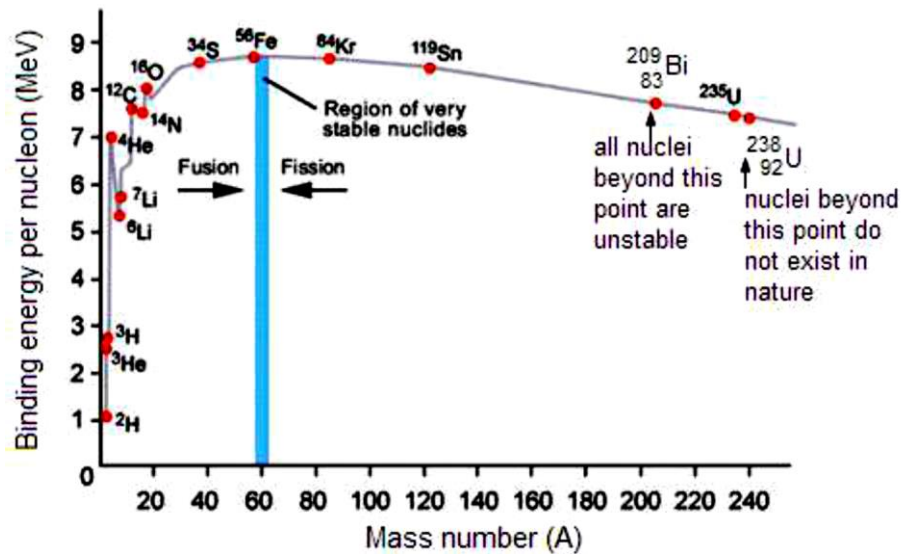


Figure 1.11: Aston curve.

b. Stability of nuclei: curve number of neutrons = f (Z: number of protons): Stability zone

The diagram represents the variation of the number of neutrons N as a function of the atomic number Z in the nuclei (Fig. 1.12).

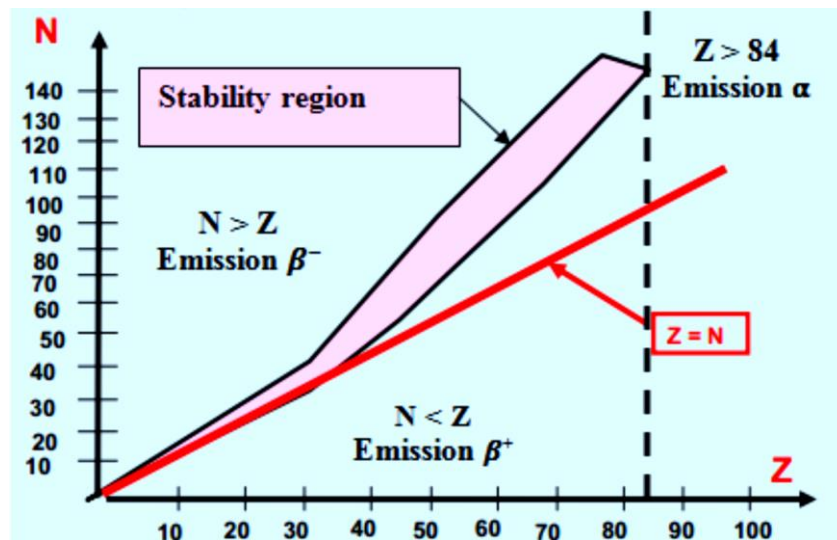


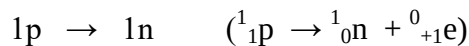
Figure 1.12: Stability diagram: number of neutrons as a function of the number of protons $N = f(Z)$.

This diagram can be summarized as follows:

- **Stable nuclei** are in the stability zone (see graph), nuclei carried by the bisector have perfect stability ($N=Z$).
- **Unstable nuclei due to excess protons ($N < Z$):**

Below the stability line

Internal nuclear reaction



Emission of β^+ particles (positron)

- **Unstable nuclei due to excess neutrons ($N > Z$):**

Above the stability line

Internal nuclear reaction



Emission β^- particles (negatron)

- **Heavy nuclei $A > 200$**

Excess number of neutrons N and protons Z . Spontaneous fission with emission of α particles (helium nucleus He).

Note:

There are nuclei with perfect stability, their number of neutrons N or their atomic number Z have particular values called **magic numbers**.

The magic numbers are: 2, 8, 20, 28, 50, 86 and 126.

Example:

He: $Z = 2$ and $N = 2$

Ni: $Z = 28$ and $N = 30$

Pb: $Z = 82$ and $N = 126$

Exercise:

Silicon Si ($Z=14$) is a mixture of three stable isotopes: ${}^{28}\text{Si}$, ${}^{29}\text{Si}$, ${}^{30}\text{Si}$; the natural isotopic abundance of the most abundant isotope is 92,23%. The average mass of natural silicon is 28,085.

1. Give the nuclear composition of each isotope.
2. Calculate the abundance of the other two isotopes.
3. Which is the most stable isotope?

Data: Masses in amu: ${}^{28}\text{Si} = 27,977$, ${}^{29}\text{Si} = 28,976$, ${}^{30}\text{Si} = 29,974$

Correction:

1. Nuclear composition of isotopes:

Isotope	$^{28}_{14}\text{Si}$	$^{29}_{14}\text{Si}$	$^{30}_{14}\text{Si}$
Protons	14	14	14
Neutrons	14	15	16

2. Calculation of: x_2 , x_3 :

The most abundant isotope is $^{28}_{14}\text{Si}$ (because its mass number $A \approx$ the average mass of Si).

$$m_{\text{Average}} = (m_1 \times x_1 + m_2 \times x_2 + m_3 \times x_3) / 100 \dots \dots \dots (1)$$

$$x_1 + x_2 + x_3 = 100\% \dots \dots \dots (2)$$

$$(2) \rightarrow x_2 = 100 - x_1 - x_3 = 100 - 92,23 - x_3 \rightarrow x_2 = 7,77 - x_3$$

$$(1) \rightarrow m_{\text{Aver}} = (m_1 \times x_1 + m_2 \times (7,77 - x_3) + m_3 \times x_3) / 100$$

$$\rightarrow x_3 = (100 \times m_{\text{Aver}} - m_1 \times x_1 - 7,77 \times m_2) / (m_3 - m_2)$$

$$x_3 = 3,04\%$$

$$\text{So: } x_2 = 7,77 - 3,04 = 4,73\%$$

3. Order of stability:

$$\Delta E/A = \Delta m \times 931,5 / A = ((Z \times m_p + N \times m_n) - m_x) \times 931,5 / A$$

$$^{28}_{14}\text{Si} : \Delta E/A = 8,189 \text{ MeV/nucleon}$$

$$^{29}_{14}\text{Si} : \Delta E/A = 8,217 \text{ MeV/nucleon}$$

$$^{30}_{14}\text{Si} : \Delta E/A = 8,275 \text{ MeV/nucleon}$$

Order of stability: $^{30}\text{Si} > ^{29}\text{Si} > ^{28}\text{Si}$, so : ^{30}Si is the most stable.

1.3. Radioactivity – Nuclear reactions

One of the main properties related to the atomic nucleus is the transformation of the nucleus into another nucleus of a different nature through nuclear reactions. The study of these transformations is radioactivity. These transformations can be either spontaneous (natural radioactivity) or induced (artificial radioactivity).

1.3.1. Types of radioactivity

1.3.1.1. 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, with the emission of radiation and particles which include three main types α , β , γ . The ability to separate these different types of radiation using electric and magnetic fields was a significant discovery in understanding the nature of radioactivity. Two of the three kinds are deflected by oppositely

charged metal plates (**Fig. 1.13**). **Alpha (α) rays** consist of positively charged particles, called **α particles**, and therefore are deflected by the positively charged plate. **Beta (β) rays**, or **β particles**, are electrons and are deflected by the negatively charged plate. The third type of radioactive radiation consists of high energy rays called **gamma (γ) rays**. Like X rays, γ rays have no charge and are not affected by an external electric or magnetic field.

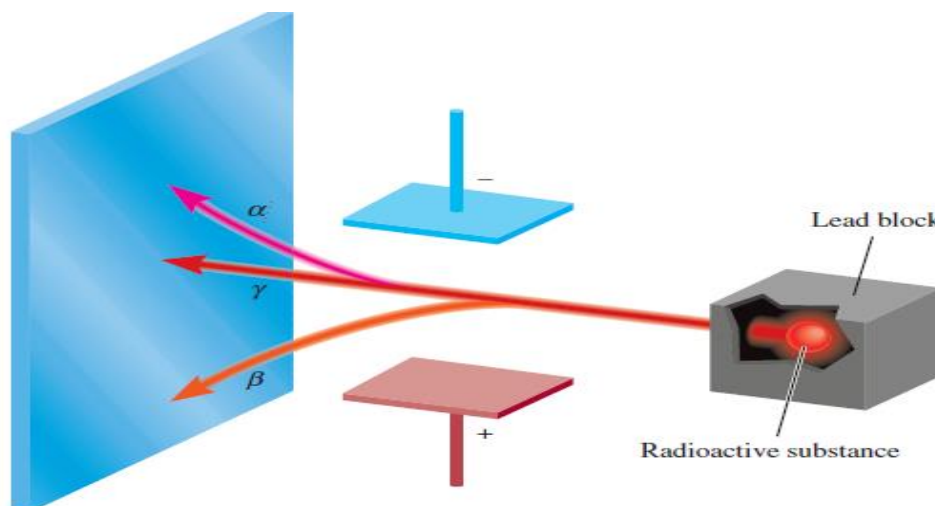


Figure 1.13: Three types of rays emitted by radioactive elements.

The nucleus that disintegrates is called the parent nucleus and the nucleus that appears is called the daughter nucleus (**Fig. 1.14**).

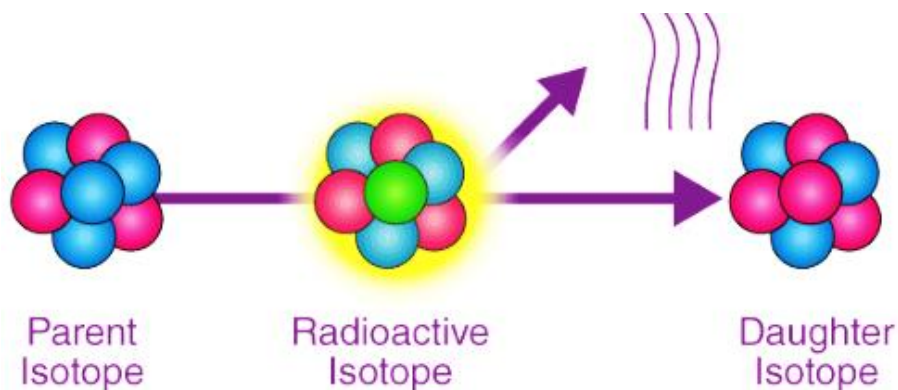


Figure 1.14: Radioactive decay.

This process is conveniently illustrated by a nuclear equation. A **nuclear equation** shows the initial nucleus to the left of the reaction arrow and the product nuclei or particles to the right of the arrow. Just as chemical equations are balanced, so are nuclear equations.

Consider the following reaction: ${}^A_Z\text{X} \longrightarrow {}^{A_1}_{Z_1}\text{Y} + {}^{A_2}_{Z_2}\text{P}$

Where: X is the parent nucleus, Y is the daughter nucleus, and P is an ejected particle. During a natural or artificial nuclear transformation, there is:

- Conservation of the total number of nucleons or mass number: **$A = A_1 + A_2$**

- Conservation of the charge number: $Z = Z_1 + Z_2$

This law is called: **Soddy and Fajans' Law of conservation**

a. Emission α

The alpha particles are helium nuclei ${}^4_2\text{He}^{2+}$ emitted by heavy nuclei (Occurs for $A \geq 200$).



The emission of an alpha particle by is illustrated in Figure 1.15 and represented by the following nuclear equation.

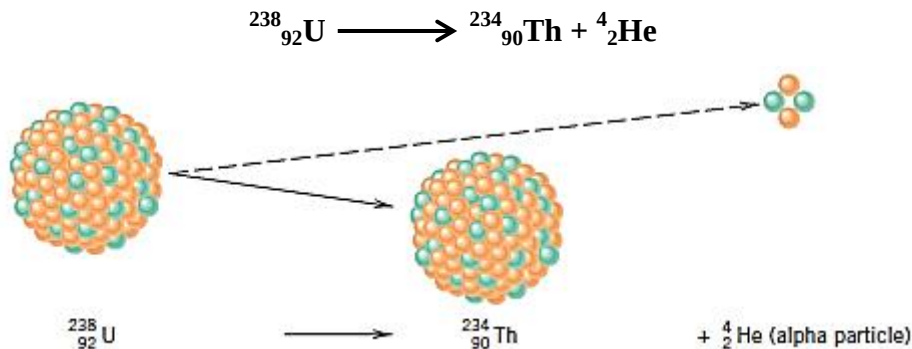


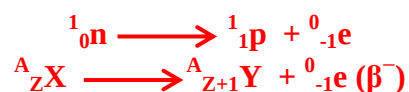
Figure 1.15: Alpha radiation

Alpha radiation is highly ionizing and thus dangerous, very energetic, and not very penetrating. Alpha particles are easily stopped by a few centimeters of air or a sheet of paper.

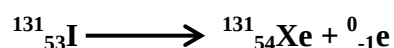
b. Emission β^-

A second form of radiation involves the emission of an electron from the nucleus. An electron emitted from the nucleus is known as a **beta (β^-) minus particle**.

β^- radioactivity affects nuclides with an excess of neutrons ($N > Z$). When there is an excess of neutrons in the nucleus, a conversion of the neutron into a proton can take place with the emission of a β^- (${}^0_{-1}\text{e}$) particle.



This type of radiation is illustrated in **Fig. 1.16** and represented by the following nuclear equation.



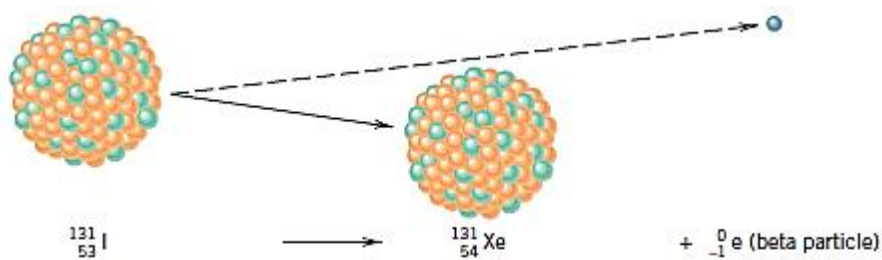


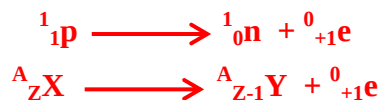
Figure 1.16: Beta radiation.

β^- radiation is highly ionizing and penetrating. It is stopped by an aluminum sheet a few millimeters thick.

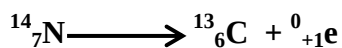
Positron Particles (β^+)

This type of radiation is not among the three types of naturally occurring radiation but is found in a few **artificially produced isotopes**. A **positron particle** is an electron with a positive charge rather than a negative charge. In effect, positron emission changes a proton into a neutron.

β^+ emission affects nuclides with an excess of protons $Z > N$. During this disintegration, there is emission of a positron $^0_{+1}\text{e}$



Example



β^+ radiation is a particle with a very short life span, it is moderately penetrating as in the case of β^- radiation

c. γ Gamma Emission

Each nucleus is characterized by a fundamental energy state. During an alpha or beta decay, the resulting daughter nucleus does not immediately reach its fundamental state; it remains in an excited state. The de-excitation of this nucleus releases a significant amount of energy in the form of electromagnetic radiation, corresponding to the emission of high-frequency photons: hence, it is a very energetic radiation.



$^A_Z\text{Y}^*$ daughter nucleus emitted in the excited state and ^A_ZY daughter nucleus de-excited (**Fig. 1.17**).

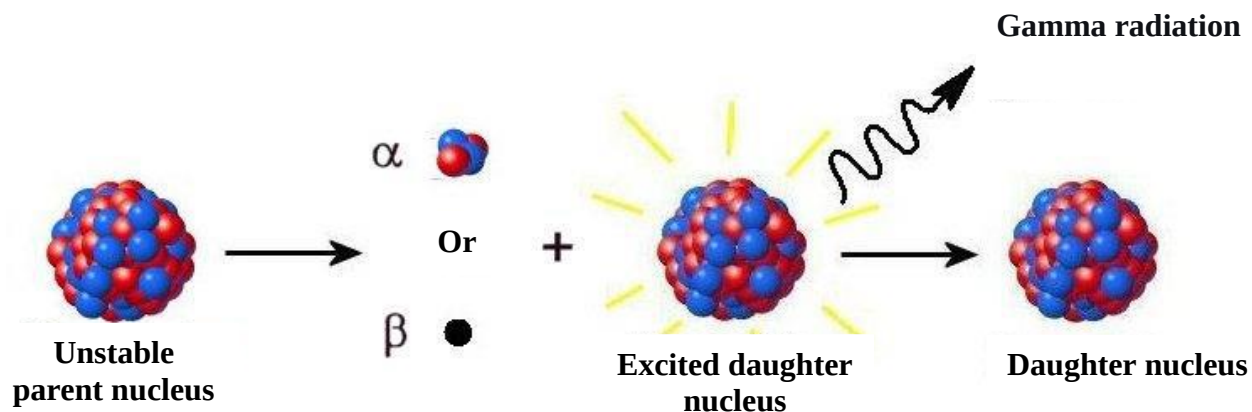
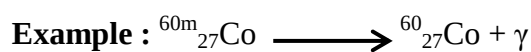


Figure 1.17: Gamma radiation.



Gamma radiation alone does not result in a change in either the mass number or the atomic number of the isotope. In the equation shown above, the **m** stands for **metastable**, which means that the isotope is in a high-energy state. A nucleus in a metastable, or high-energy, state may emit energy in the form of gamma radiation.

The product nucleus has the same identity but is then in a lower energy state.

γ radiation is less ionizing and very penetrating; a thick layer of concrete or lead is required to protect against it (Fig. 1.18).

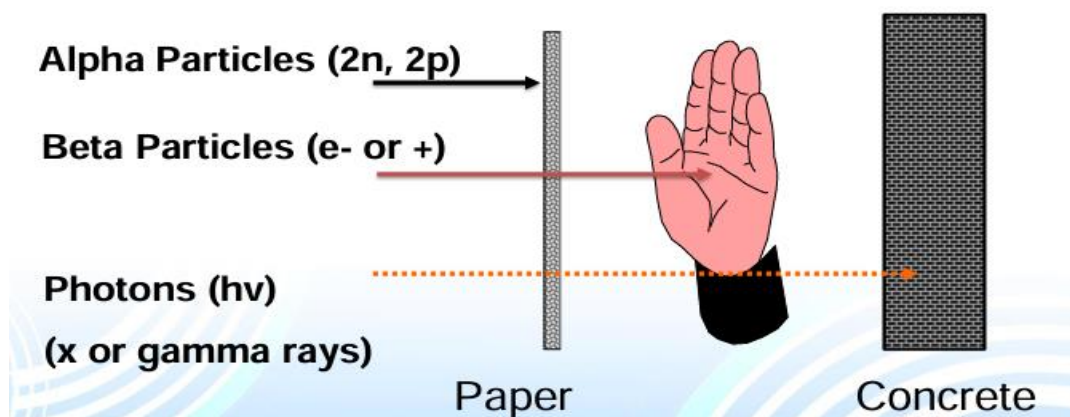


Figure 1.18: Radiation Types.

1.3.1.2. Artificial radioactivity and nuclear reactions

Artificial radioactivity (also known as induced radioactivity) is the process by which a stable, naturally non-radioactive material is made radioactive by bombarding it with high energy particles or radiation such as neutron, proton, deuteron, and α particle. This is achieved

through artificial means, typically in a nuclear reactor or a particle accelerator. This phenomenon was first discovered in 1934 by Irène Joliot-Curie and Frédéric Joliot-Curie. They bombarded aluminum foil with alpha particles, creating a new radioactive isotope of phosphorus.



There are three types of nuclear reactions: nuclear transmutation, nuclear fission and nuclear fusion.

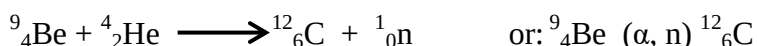
a. Transmutation reactions

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

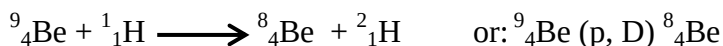
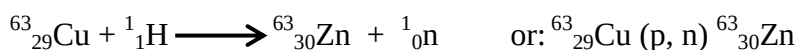
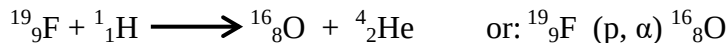
a.1. Transmutation by helium



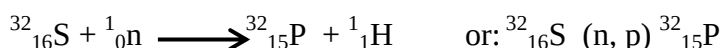
This reaction can be written in abbreviated notation: ${}^{14}_7\text{N} (\alpha, p) {}^{17}_8\text{O}$



a.2. Transmutation by proton



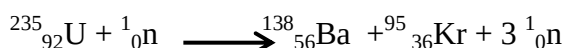
a.3. Transmutation by neutron



b. Fission reaction

Under neutron bombardment, a heavy nucleus undergoes fission, splitting into two lighter nuclei. However, these two nuclei are obtained in their excited states, and they, in turn, emit or release neutrons, leading to the possibility of a nuclear chain reaction (**Fig. 1.19**).

Example



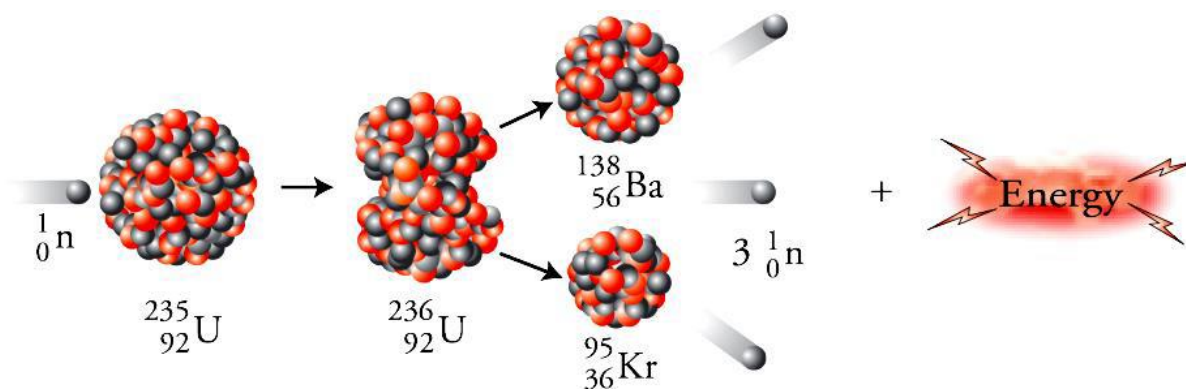
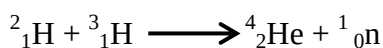


Figure 1.19: Nuclear fission

c. Fusion reaction

It is the union of two light nuclei into a heavier nucleus with the release of a considerable amount of energy. Among the known fusion reaction we can cite (Fig. 1.20):

Example



It was even suggested that this was the major source of energy in the universe because it powered the sun and the stars.

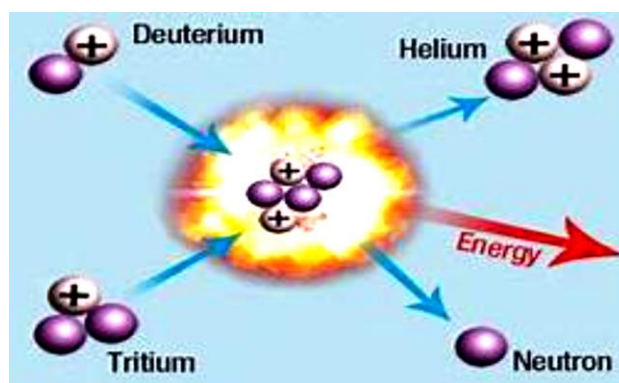


Figure 1.20: Nuclear fusion

Nuclear fusion is the principle of thermonuclear bombs (H bombs or hydrogen bombs).

1.3.2. Kinetics of radioactive decay

1.3.2.1. Law of radioactive disintegration

This law applies to both natural and artificial radioactive nuclides. In a given sample, the number of radioactive atoms varies over time. Radioactive decay depends neither on pressure, temperature, nor the chemical compounds in which the radioactive atoms are involved. The aim is to determine the statistical evolution of the number N of radioactive nuclides present in

a sample. This involves establishing the mathematical equation for the decrease in N as a function of time t (**Fig. 1.21**).

Given the radioactive decay: $A^* \rightarrow B$ where B is stable.

Experience shows that the number of radioactive atoms that decay is proportional to the number of unstable atoms (N) present at the given time (t)

The decay rate is written as: $-dN/dt = \lambda \times N$

After integration: $\ln (N/N_0) = -\lambda t \rightarrow N/N_0 = e^{-\lambda t}$

The decay law is written as follows:

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

With:

N: number of unstable nuclei remaining at time (t).

N_0 : number of unstable nuclei at the initial time (t = 0).

λ : decay constant or radioactive constant (s^{-1} , min^{-1} , h^{-1} , $year^{-1}$)

$N = n \times N_A$

$$n \times N_A = n_0 \times N_A e^{-\lambda t} \Rightarrow n = n_0 e^{-\lambda t}$$

$$1 \text{ mol} \longrightarrow N_A$$

$$n \text{ mol (m/M)} \longrightarrow N$$

$$\text{So: } N = n \times N_A = m \times N_A / M \quad ; \text{ and; } N_0 = m_0 \times N_A / M$$

We replace N and N_0 by their formulas; it results that:

$$(m \times N_A / M) = (m_0 \times N_A / M) \times e^{-\lambda t} \text{ so ; } m = m_0 e^{-\lambda t}$$

With:

n: number of moles of the radioactive element at time $t \neq 0$

n_0 : number of moles of the radioactive element at time $t=0$

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

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

Number of nuclei decayed:

$$N' = N_0 - N = N_0 - N_0 e^{-\lambda t} = N_0 (1 - e^{-\lambda t}) \Rightarrow N' = N_0 (1 - e^{-\lambda t})$$

N' : Number of nuclei decayed

Mass of decayed nuclei:

$$m' = m_0 - m = m_0 - m_0 e^{-\lambda t} = m_0 (1 - e^{-\lambda t}) \Rightarrow m' = m_0 (1 - e^{-\lambda t})$$

m' : mass of decayed nuclei

1.3.2.2. Radioactive constant

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

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

1.3.2.3. Half-life time: ($t_{1/2}$)

Half-life (often denoted as $t_{1/2}$ or T) is the time required for half of the atoms of a radioactive material to decay to another nuclear form.

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

When: $t = t_{1/2} \Rightarrow N = N_0 / 2$

Therefore: $(N_0 / 2) = N_0 e^{-\lambda T} \rightarrow e^{-\lambda T} = (1/2) \Rightarrow \ln(e^{-\lambda T}) = \ln(1/2)$

$-\lambda T = \ln(1/2) \Rightarrow \ln(1/2) = -\ln 2 \Rightarrow -\lambda T = -\ln 2$

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

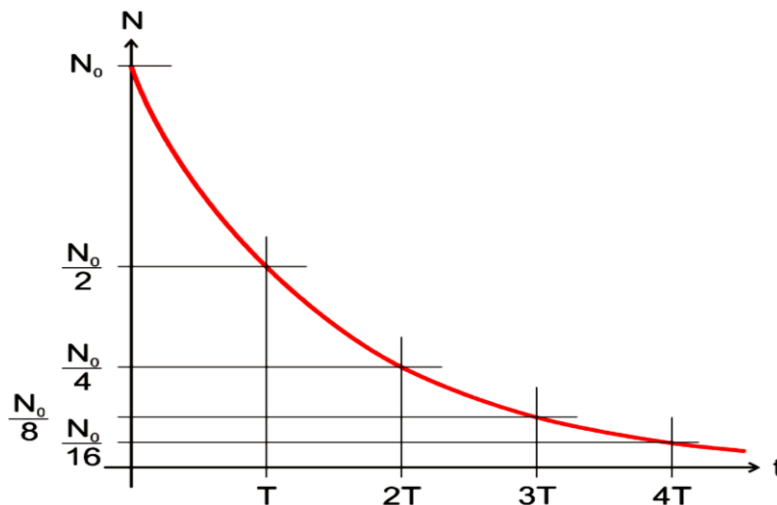


Figure 1.21: Statistical evolution of the number $N = f(t)$

1.3.2.4. Activity A

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

$A = -dN/dt = \lambda \times N$

$$A = \lambda \times N$$

Units

- Disintegration per second (dps).
- Disintegration per minute (dpm).
- Disintegration per hour (dph).
- The **Becquerel (Bq)** : 1 Bq = 1 dps
- The **Curie (Ci)** : 1Ci = $3,7 \times 10^{10}$ dps = $3,7 \times 10^{10}$ Bq

We also have the law of activity which is expressed by the following relation:

$$N = N_0 \times e^{-\lambda t} \implies \lambda \times N = \lambda \times N_0 e^{-\lambda t} \implies \boxed{A = A_0 \times e^{-\lambda t}}$$

With:

A: Activity at time $t \neq 0$.

A_0 : Initial activity at time $t=0$

1.3.3. Energy of a Nuclear Reaction

The energy of a nuclear reaction is a measure of the total energy released or absorbed when the reaction occurs. It is based on the fundamental principle of mass-energy equivalence from Einstein's theory of relativity:

$$\boxed{E = \Delta m \times C^2}$$

E: Energy released or absorbed (in joules, J),

Δm : mass defect (in kilograms, kg),

C: speed of light in vacuum (3×10^8 m/s).

$$\boxed{\Delta m = \sum \text{mass of reactants} - \sum \text{mass of products}}$$

Example 1: Fission of uranium 235



Masses (amu): $m_{\text{U}} = 235,0439$, $m_{\text{n}} = 1,0087$, $m_{\text{Ba}} = 137,905247$, $m_{\text{Kr}} = 94,939356$.

$$\Delta m = \sum m_{\text{reactants}} - \sum m_{\text{products}} = (m_{\text{U}} + m_{\text{n}}) - (m_{\text{Ba}} + m_{\text{Kr}} + 3m_{\text{n}})$$

$$\Delta m = 236,0525948 - 235,8705977 = 0,1819971 \text{ amu}$$

Energy released

$$E = \Delta m \times 931,5 \approx 0,1819971 \times 931,5 \approx 169,53029 \text{ MeV}$$

Example 2: ${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^4_2\text{He}$

$$m_{\text{Ra}} = 226,0254 \text{ amu}, \quad m_{\text{Rn}} = 222,0175 \text{ amu}, \quad m_{\text{He}} = 4,0039 \text{ amu}$$

$$\Delta m = m_{\text{Ra}} - (m_{\text{Rn}} + m_{\text{He}}) = 226,0254098 - 226,0201795 = 0,0052303 \text{ amu}$$

$$E = \Delta m \times 931,5 = 0,0052303 \times 931,5 = 4,87 \text{ MeV for one nucleus.}$$

$$E = E \times N_A = 4,87 \times 6,022 \times 10^{23} = 29,37142 \times 10^{23} \text{ MeV for one mole of nuclei.}$$

1.3.4. Applications of Radioactivity

Radioactivity has several important applications across various fields. Here are some of the key applications:

- **Medical Applications**

Radiotherapy: Used to treat cancer by targeting and destroying malignant cells.

Diagnostic Imaging: Techniques like PET (Positron Emission Tomography) and SPECT (Single Photon Emission Computed Tomography) use radioactive isotopes to visualize organs and tissues.

- **Nuclear Power**

Energy Production: Nuclear reactors use radioactive isotopes (like uranium 235) to produce energy through nuclear fission. This energy produces steam that drives turbines to generate electricity for cities and industries.

- **Research**

Tracer Studies: Radioactive isotopes serve as tracers in biochemical and environmental studies to track the movement of substances.

Radiometric Dating: Techniques like carbon dating use radioactive decay to estimate the age of archaeological and geological samples.

- **Agriculture**

Food Irradiation: Used to kill bacteria and pests in food, extending shelf life and ensuring safety.

Mutation Breeding: Radioactive isotopes induce mutations in plants to develop new varieties with desirable traits.

1.3.5. Dangers of Radioactivity

When not properly managed or when deployed for harmful purposes, radioactivity poses a significant threat to human health. The danger arises as alpha, beta, and gamma radiation passes through living tissue, ionizing atoms and molecules and triggering abnormal chemical reactions.

The consequences of exposure can be immediate or delayed for years. At the cellular level, radiation can damage crucial macromolecules like DNA and RNA, leading to cancer, compromising the immune system, and causing genetic mutations that alter cell function or destroy cells entirely. Furthermore, radioactive fallout introduces unstable nuclides into the environment, which are absorbed by plants and bioaccumulate through the food chain.

An additional indirect hazard is the radiolysis of water, where radiation ionizes water molecules to produce highly toxic free radicals. Although the body possesses natural repair mechanisms to eliminate or neutralize damaged cells, any exposure that affects critical tissues can lead to irreversible damage, even at low doses.

Exercise

Consider the decay reaction of thorium: $^{232}_{90}\text{Th} \longrightarrow ^{228}_{88}\text{Ra} + \dots\dots\dots$

1. Complete the reaction and identify the type of radiation emitted by this nucleus.
2. If the initial mass of thorium is 20 g, what will be its mass after a time equal to 5 times the half-life?
3. After a time equal to 10 hours, it is observed that 80% of the thorium nucleus disintegrates. Calculate the radioactive constant and the half-life of thorium.

Correction

1. The decay reaction is: $^{232}_{90}\text{Th} \longrightarrow ^{228}_{88}\text{Ra} + ^4_2\text{He}$

Emitted particle: Helium nucleus ^4_2He (alpha particle, α).

Type of decay: Alpha decay (loss of 4 mass units and 2 atomic numbers confirms this).

2. Mass after 5 half-lives:

Initial mass $m_0 = 20$ g

After $n=5$ half-lives, the remaining mass is:

$$m = m_0 (1/2)^n = 20(1/2)^5 = 20 \times 1/32 = 0,625 \text{ g}$$

3. Calculate the decay constant (λ) and half-life ($t_{1/2}$):

Given: Time $t = 10$ hours,

80% decayed $\rightarrow$ 20% remaining ($N = 0,2 N_0$).

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

$$0,2N_0 = N_0 e^{-10\lambda} \Rightarrow 0,2 = e^{-10\lambda}$$

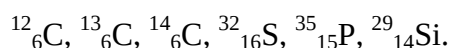
$$\text{Ln}(0,2) = -10\lambda \Rightarrow \lambda = -(\text{Ln}(0,2))/10 = 0,16094 \text{ h}^{-1}.$$

- Calculate half-life ($t_{1/2}$): $t_{1/2} = \frac{\text{Ln } 2}{\lambda} = 4,31 \text{ h}$

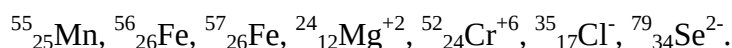
Exercises

Exercise 1

- 1) Give the nuclear composition of the following elements:



- 2) Give the number of electrons, protons and neutrons for the following atoms and ions:



- 3) Four nuclides A, B, C, and D have nuclei constituted as indicated below:

	A	B	C	D
Number of protons	21	22	22	20
Number of neutrons	26	25	27	27
Mass number	47	47	49	47

Are there any isotopes among these four nuclides?

- 4) Sulfur is a mixture of four isotopes with respective masses equal to 31,972 amu, 32,971 amu, 33,968 amu, and 35,967 amu, and with abundances of 95,0 %, 0,76 %, and 4,22 % for three of them.
- Calculate the abundance of the fourth isotope.
 - Calculate the average atomic mass of sulfur.

Exercise 2

The masses of the proton, neutron and electron are $1,6723842 \times 10^{-24}$ g, $1,6746887 \times 10^{-24}$ g and $9,109534 \times 10^{-28}$ g respectively.

- Define the atomic mass unit (amu). Give its value in g with the same significant figures as the masses of particles of the same order of magnitude.
- Calculate in amu and to the nearest 10^{-4} , the masses of the proton, the neutron and the electron.
- Calculate in amu the masses of the nucleus and the atom of $^{40}_{20}\text{Ca}$. Conclude.

Exercise 3

I) Natural bromine is a mixture of two isotopes, ^{79}Br and ^{81}Br , whose atomic masses are 78,9183 amu and 80,9163 amu respectively. Knowing that the effective atomic mass of

bromine is 79,904 amu, calculate the natural abundances of the two isotopes present in natural bromine.

II) An element A_ZX : m_1 , 44 neutrons and 35 electrons, $\frac{E_L}{A_1} = 8,46$ MeV/nucleon. Calculate

the mass m_1 in atomic mass unit (amu) of this element.

2. Compare the stability of A_ZX with ${}^{A2}_{19}K$ ($m_2 = 39,9640$ amu, $\Delta m = 0,3559$ amu)

Exercise 4

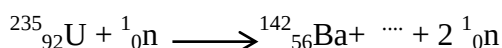
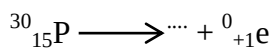
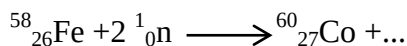
Potassium ($Z = 19$) exists in the form of three isotopes: ${}^{39}K$, ${}^{40}K$ and ${}^{41}K$ whose respective masses are: 38,9635 amu; 39.9640 amu and 40,9618 amu.

The ${}^{40}K$ isotope is the rarest; its natural abundance is 0,012%. Knowing that the average mass of natural potassium is 39,102 amu:

- 1) Calculate the natural abundances of isotopes 39 and 41 in natural potassium.
- 2) Give the nuclear composition of each isotope.
- 3) Calculate the binding energy of each isotope in joules and MeV.
- 4) Give, with justification, the order of stability of the nuclei of the three isotopes.

Exercise 5

Complete the nuclear reactions:



Exercise 6

The radioactive radon ${}^{222}_{86}Rn$ emits α particles with a period $T = 3,76$ days.

- 1) Write the nuclear decay reaction.
- 2) Calculate the initial mass m_0 of the sample, given that its initial activity is $A_0 = 4,7 \cdot 10^3$ Ci.
- 3) Calculate the activity of the sample at time $t = 20$ days.
- 4) Determine the time t at which its activity would have decreased by 35%.

Data : $N_A = 6,022 \cdot 10^{23}$, $1 \text{ Ci} = 3,7 \cdot 10^{10} \text{ dps}$

Exercise 7

Let there be an element X that decays into an element Y and a negaton β^- . Given that the atomic number of Y is 28 and the nucleus of X contains 33 neutrons:

- 1) Write the nuclear decay reaction.
- 2) Knowing that we initially have 0,012 kg of element X and that after 15 days we have obtained $9,0345 \cdot 10^{22}$ β^- particles, determine the half-life of element X.
- 3) Determine the activity in curies of element X after 30 days.

Correction

Exercise 1

1) Nuclear Composition of the Following Elements:

The nuclear composition refers to the number of protons (p) and neutrons (n) in the nucleus.

Element	$^{12}_6\text{C}$	$^{13}_6\text{C}$	$^{14}_6\text{C}$	$^{32}_{16}\text{S}$	$^{35}_{15}\text{P}$	$^{29}_{14}\text{Si}$
Number of protons	6	6	6	16	15	14
Number of neutrons	6	7	8	16	20	15

2) Number of Electrons, Protons, and Neutrons:

Atom/ion	Protons	Neutrons	Electrons
$^{55}_{25}\text{Mn}$	25	$55 - 25 = 30$	25
$^{56}_{26}\text{Fe}$	26	$56 - 26 = 30$	26
$^{57}_{26}\text{Fe}$	26	$57 - 26 = 31$	26
$^{24}_{12}\text{Mg}^{+2}$	12	$24 - 12 = 12$	$12 - 2 = 10$
$^{52}_{24}\text{Cr}^{+6}$	24	$52 - 24 = 28$	$24 - 6 = 18$
$^{35}_{17}\text{Cl}^{-}$	17	$35 - 17 = 18$	$17 + 1 = 18$
$^{79}_{34}\text{Se}^{2-}$	34	$79 - 34 = 45$	$34 + 2 = 36$

3) Isotopes are atoms of the same element (same number of protons) with different numbers of neutrons (and thus different mass numbers).

- Nuclides B and C both have 22 protons but different mass numbers (47 and 49). Therefore, B and C are isotopes.
- No other pairs share the same atomic number.

Sulfur Isotopes:

a) Abundance of the Fourth Isotope:

$$x_1 + x_2 + x_3 + x_4 = 100 \%$$

$$x_4 = 100 - (95,0 + 0,76 + 4,22) = 0,02 \%$$

b) Average Atomic Mass of Sulfur:

$$\text{Average mass} = \frac{\sum m_i \times x_i}{100}$$

$$\text{Average mass} = [(31,972 \times 95) + (32,97 \times 4,22) + (33,968 \times 0,76) + (35,967 \times 0,02)] = 32,03 \text{ amu}$$

Exercise 2

1) Definition of the Atomic Mass Unit (amu)

The atomic mass unit (amu) is defined as exactly one-twelfth of the mass of a carbon 12 atom.

In grams, its value is: **1u.m.a = $1,660539067 \times 10^{-24}$ g**

2) Masses of proton, neutron, and electron in amu using the conversion:

Mass in amu = Mass in grams / $1,660539067 \times 10^{-24}$

$$m_p = 1,00727 \text{ amu}$$

$$m_n = 1,00866 \text{ amu}$$

$$m_e = 0,00055 \text{ amu}$$

3) Masses of the Nucleus and Atom of $^{40}_{20}\text{Ca}$ Calcium

$^{40}_{20}\text{Ca}$ has: 20 protons, 20 neutrons, and 20 electrons.

a) Mass of the Nucleus

$$m_{\text{nucleus}} = 20 \times 1,007277 + 20 \times 1,008665 = 40,31884 \text{ amu}$$

b) Mass of the Atom

$$m_{\text{Atom}} = m_{\text{nucleus}} + Zm_e = 40,31884 + 20 \times 0,000549 = 40,32982 \text{ amu} = 6,695968 \times 10^{-23} \text{ g}$$

Conclusion: $m_{\text{Atom}} \approx m_{\text{nucleus}}$ ($m_e \ll m_p + m_n$), the mass of the atom is located in the nucleus.

Exercise 3

I) ^{79}Br : $m_1 = 78,9183 \text{ amu}$, $x_1 = ?$

^{81}Br : $m_2 = 80,9163 \text{ amu}$, $x_2 = ?$

Average mass = 79,904 amu

$$\begin{cases} x_1 + x_2 = 100 \% \longrightarrow x_2 = 100 - x_1 \\ \text{Average mass} = (m_1x_1 + m_2x_2)/100 \end{cases}$$

$$x_1 = 100(\text{Average mass} - m_2)/(m_1 - m_2)$$

$$x_1 = 50,66 \%, x_2 = 49,34 \%$$

II) Identify the element and its nucleon composition

The element has: 35 electrons $\rightarrow$ atomic number $Z=35$

44 neutrons $\rightarrow$ neutron number $N=44$

$$\text{Mass number } A_1 = Z + N = 35 + 44 = 79$$

The binding energy per nucleon is: $\frac{\Delta E}{A_1} = \frac{BE}{A_1} = 8,46 \text{ MeV/nucleon}$

$$\text{Binding energy: } BE = \Delta E = 8,46 \times A_1 = 79 \times 8,46 = 668,34 \text{ MeV}$$

$$\Delta E = \Delta m \times 931,5 \longrightarrow \Delta m = \Delta E / 931,5 = 0,71749 \text{ amu}$$

$$m_1 = Zm_p + Nm_n - \Delta m = 78,918 \text{ amu}$$

The stability of nuclei

$$m_2 = 39,9640 \text{ amu} \longrightarrow A_2 = 40$$

$$\Delta E_2 / A_2 = \Delta m_2 \times 931,5 / A_2 = 8,29 \text{ MeV/nucleon}$$

$$\Delta E_1 / A_2 > \Delta E_2 / A_2 \longrightarrow {}^{79}_{35}\text{X is more stable than } {}^{49}_{19}\text{K}$$

Exercise 4

1) The natural abundances of isotopes 39 and 41 in natural potassium

$$\left\{ \begin{array}{l} x_1 + x_2 + x_3 = 100 \% \longrightarrow x_3 = 100 - x_1 - x_2 = 99,988 - x_1 \\ \text{Average mass} = (m_1 \times x_1 + m_2 \times x_2 + m_3 \times x_3) / 100 \end{array} \right.$$

$$x_1 = (\text{Average mass} \times 100 - m_2 \times x_2 - 99,988 \times m_3) / (m_1 - m_3)$$

$$x_1 = 93,072 \%, x_3 = 6,916 \%$$

2) The nuclear composition of each isotope

Isotope	${}^{39}_{19}\text{K}$	${}^{40}_{19}\text{K}$	${}^{41}_{19}\text{K}$
Protons	19	19	19
Neutrons	20	21	22

3) The binding energy of each isotope in joules and MeV

$$\Delta E = \Delta m \times 931,5 = (Z \times m_p + N \times m_n - m_{\text{nucleus}}) \times 931,5$$

$${}^{39}_{19}\text{K} : \Delta E = 324,18 \text{ MeV}$$

$${}^{40}_{19}\text{K} : \Delta E = 331,977 \text{ MeV}$$

$${}^{41}_{19}\text{K} : \Delta E = 342,102 \text{ MeV}$$

4) The order of stability of the nuclei of the three isotopes.

$${}^{39}_{19}\text{K} : \Delta E / A = 8,312 \text{ MeV/nucleon}$$

$${}^{40}_{19}\text{K} : \Delta E / A = 8,299 \text{ MeV/nucleon}$$

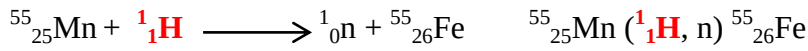
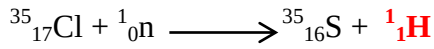
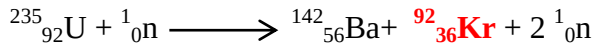
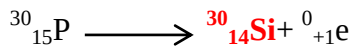
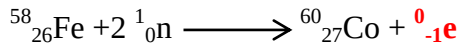
$${}^{41}_{19}\text{K} : \Delta E / A = 8,343 \text{ MeV/nucleon}$$

The higher the binding energy per nucleon, the more stable the nucleus. Thus:

$${}^{41}\text{K} > {}^{39}\text{K} > {}^{40}\text{K} \longrightarrow {}^{41}\text{K is the more stable.}$$

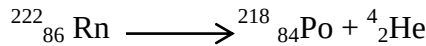
Exercise 5

Complete the nuclear reactions:



Exercise 6

1) Nuclear decay reaction



2) Initial mass m_0

$$A_0 = \lambda \times N_0 ; \lambda = \text{Ln}2/T ; N_0 = n_0 \times N_A = m_0 \times N_A/M$$

$$m_0 = (A_0 \times T \times M) / (N_A \times \text{Ln}2) = (4,7 \times 10^3 \times 3,7 \times 10^{10} \times 3,76 \times 24 \times 3600 \times 222) / (\text{Ln} 2 \times 6,022 \times 10^{23})$$

$$m_0 = 0,03 \text{ g}$$

3) Activity at $t = 20$ days

$$A = A_0 e^{-\lambda t} = 4,7 \times 10^3 e^{-(\text{Ln}2/3,76) \times 20} = 117,73 \text{ Ci}$$

4) Time When Activity Decreases by 35%

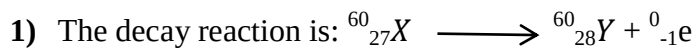
$$A = A_0 e^{-\lambda t} \longrightarrow t = (T/\text{Ln}2) \times \text{Ln}(A_0/A) \quad A = 0,65 A_0$$

$$t = 2,337 \text{ days}$$

Exercise 7

Atomic number of Y is 28 $\rightarrow$ Atomic number of X is $Z=27$.

Nucleus of X contains 33 neutrons $\rightarrow$ Mass number $A=27+33 = 60$.



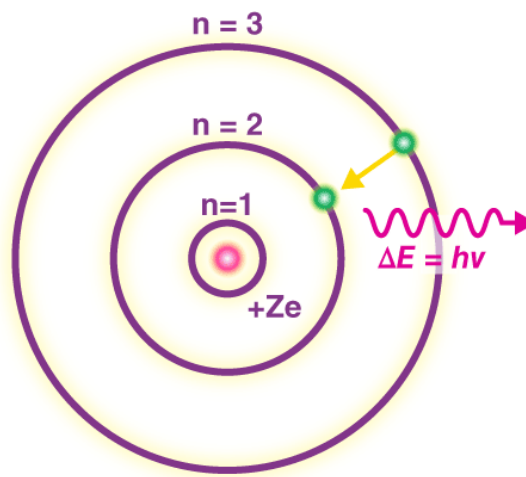
2) The half-life of element X

$$T = \text{Ln}2/\lambda, \lambda = \frac{1}{t} \times \text{Ln}\left(\frac{N_0}{N}\right) = \frac{1}{t} \times \text{Ln}\left(\frac{\frac{m_0 \times N_A}{M}}{\frac{m_0}{M} \times N_A - N_d}\right) = \frac{1}{15} \times \text{Ln}\left(\frac{\frac{12}{60} \times 6,022 \times 10^{23}}{\frac{12}{60} \times 6,022 \times 10^{23} - 9,0345 \times 10^{22}}\right)$$

$$\lambda = 0,0924 \text{ days}^{-1}. T = 7,5 \text{ days.}$$

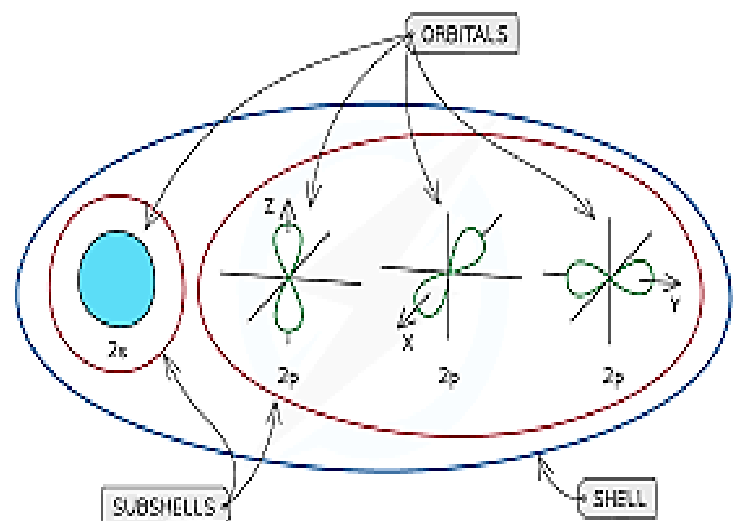
3) Activity After 30 Days

$$A = A_0 e^{-\lambda t} = \lambda \times N_0 e^{-\lambda t} = (\text{Ln}2/T) \times (m_0/M) \times N_A e^{-\lambda t} = 8,05 \times 10^{15} \text{ dps} = 2,17 \text{ Ci.}$$



Chapter 2

Quantification of energy



Chapter 2

Quantification of energy

2.1. Wave-particle duality

2.1.1. Wave aspect of light: electromagnetic or light wave

Electromagnetic radiation refers to any form of energy capable of propagating through a vacuum. The heat from a fire, sunlight, X-rays used in medicine, and the energy used to cook food in a microwave oven are all forms of electromagnetic radiation. Although these energy sources may seem very different from each other, they all share the common characteristic of behaving like waves. Atoms are also examples of electromagnetic radiation, exhibiting the same type of wave-like behavior and traveling through a vacuum at the speed of light.

Light rays are characterized by the propagation of an electromagnetic wave at the speed of light ($C = 3 \times 10^8 \text{ m/s}$).

Four parameters characterize a wave (**Fig. 2.1**):

- ✓ **The speed of propagation in a vacuum, C:** a wave travels at the speed of light, which is $3 \times 10^8 \text{ m} \cdot \text{s}^{-1}$.
- ✓ **The wavelength, λ (lambda):** represents the distance between two consecutive crests (or two consecutive troughs); it is expressed in meters (m); $\lambda = \frac{c}{\nu}$
- ✓ **The frequency ν (nu):** corresponds to the number of wavelengths passing a reference point each second; the SI unit of frequency is the hertz (Hz), which is one wavelength per second (s^{-1});
- ✓ **The amplitude:** represents the intensity of the radiation.

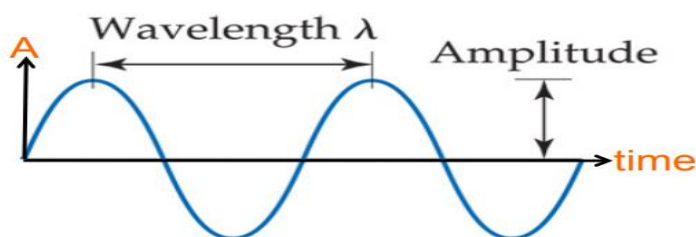


Figure 2.1: Wave's characterization

The spectrum of all radiations can be presented as follows (**Fig. 2.2**):

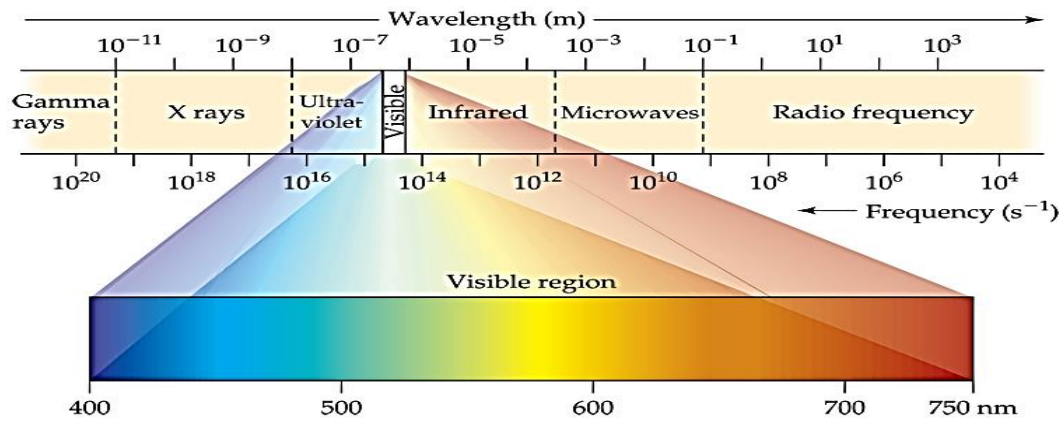


Figure 2.2: Radiations spectrum.

2.1.2. Particle aspect of light: photoelectric effect

In 1886, the German physicist Heinrich Rudolf Hertz experimentally demonstrated that a metallic material exposed to light could emit negatively charged particles (electrons). This discovery was named the **photoelectric effect** (Fig. 2.3).

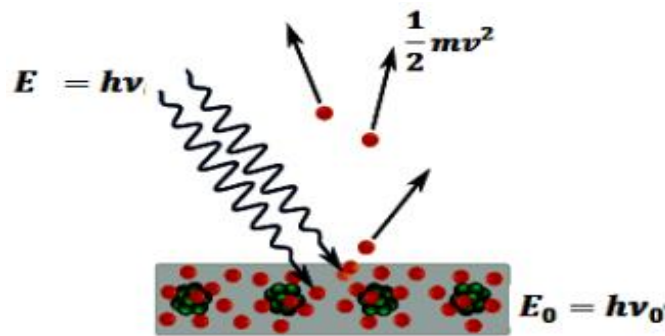


Figure 2.3: Photoelectric effect.

$h\nu$: incident irradiation energy.

$h\nu_0$: electron extraction energy.

To eject electrons from a metallic surface subjected to electromagnetic radiation, an energy E_0 , called the extraction energy or photoelectric threshold energy must be supplied:

$$E_0 = h \times \nu_0$$

Three cases may be observed depending on the irradiated metal:

- If $h\nu < h\nu_0$: The incident radiation is insufficient to extract (eject) electrons from the metal.
- If $h\nu = h\nu_0$: The incident radiation is just sufficient to extract electrons from the metal (corresponding to the ionization energy of the metal).

- If $h\nu > h\nu_0$: The incident radiation extracts electrons from the metal, and the excess energy is converted into kinetic energy (E_k) of the electrons:

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

To interpret the photoelectric effect, Einstein proposed that the energy carried by a light wave does not flow continuously but travels in packets or quanta of energy, also called "**photons**".

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

h : Planck's constant; $h = 6,62 \times 10^{-34}$ J.s

ν : frequency Hz or s^{-1}

C : speed of light $C = 3 \times 10^8$ m/s

λ : wavelength.

2.2. Interaction between light and matter

2.2.1. Emission spectrum of the hydrogen atom

Experimentally, the emission spectrum of the hydrogen atom is obtained by placing tube containing hydrogen at low pressure in front of the slit of a spectrograph and applying an electric discharge. This discharge dissociates the molecules and excites the hydrogen atoms. As the atoms return from various excited states to lower energy levels, electromagnetic radiation is emitted. The excited hydrogen atoms emit a pinkish light (**Fig. 2.4**).

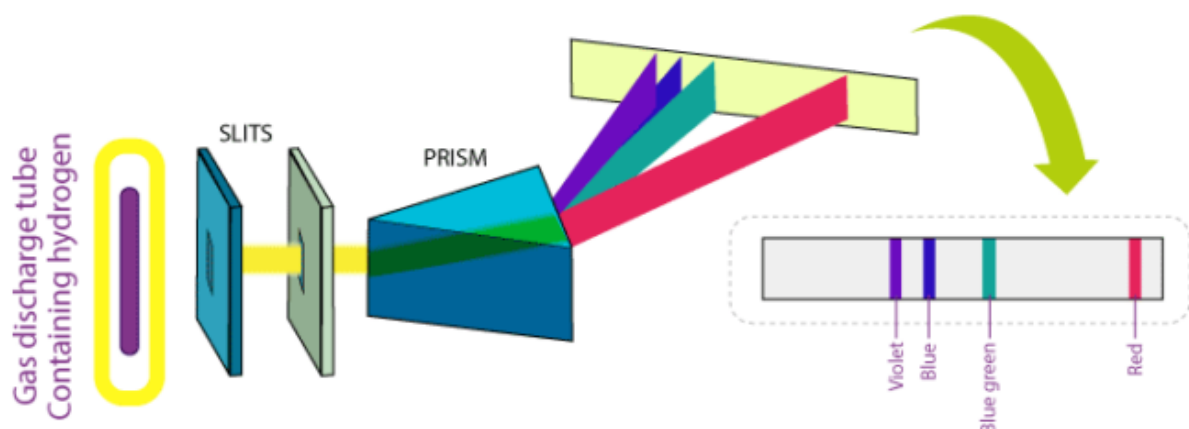


Figure 2.4: Spectrum of the hydrogen atom.

Four lines are observed in the visible part of the emission spectrum: red at 656,3 nm, blue-green at 486,1 nm, blue violet at 434,1 nm and violet at 410,2 nm.

The photographic plate shows a spectrum of discontinuous lines and each line corresponds to a frequency ν and therefore to a wavelength λ characteristic of hydrogen.

2.2.2. Balmer-Rydberg empirical relationship

As early as 1885, Rydberg proposed an empirical relation (mathematical relationship derived from experimental data) giving the wave numbers of the spectral lines in the Balmer series:

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

Where:

$\bar{\nu}$: wavenumber

ν : frequency of light

R_H : Rydberg constant for hydrogen. $R_H = 1,096\,776 \times 10^7 \text{ m}^{-1}$

λ : Wavelength ;

n : : Natural number, such that $n > 2$

Ultraviolet (UV) and Infrared (IR) radiations are also emitted by hydrogen. These spectral lines were discovered by **Lyman** (UV), **Paschen** (IR), **Brackett** (IR), and **Pfund** (IR).

2.2.3. Concept of spectral series

Ritz generalized the Balmer-Rydberg formula to all spectral lines in the hydrogen emission spectrum according to the relation:

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

The observed spectrum will form groups of spectral lines (**Fig 2.5**). Each group of lines is called a "series" and is named after the researcher who discovered it (**Table 2.1**).

Table 2.1: Spectral series

n_1	1	2	3	4	5
n_2	≥ 2	≥ 3	≥ 4	≥ 5	≥ 6
Name of the series	Lyman 1906	Balmer 1885	Paschen 1909	Brackett 1922	Pfund 1924
Spectral range	UV	Visible	Near IR	Fair IR	

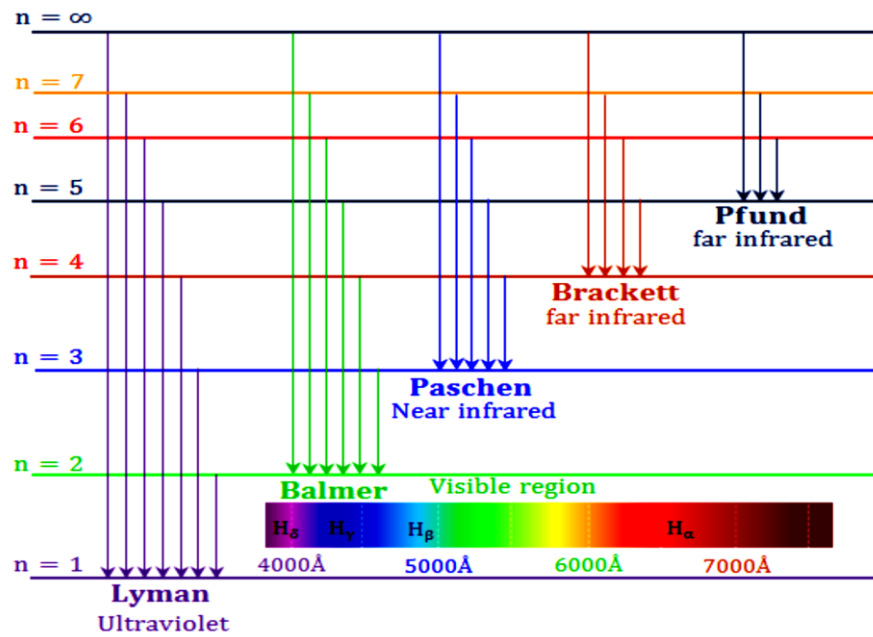


Figure 2.5 : Hydrogen spectral series.

Note

Each series is bounded by two lines:

- **The first line** corresponds to the **transition** $n_2 \longrightarrow n_1$ with $n_1 = n$ and $n_2 = n+1$. It is characterized by a **smaller energy difference** and **greater wavelength** ($\lambda_{\max}$).

$$\lambda_{\max} = \frac{1}{R_H} \times \frac{n^2(n+1)^2}{(n+1)^2 - n^2} \implies \lambda_{\max} = \frac{n^2(n+1)^2}{(2n+1)R_H}$$

- **The final line** corresponds to the **transition** $n_2 = \infty \longrightarrow n_1$ with $n_1 = n$ and $n_2 = \infty$. It is characterized by **greater energy difference** and **smaller wavelength** ($\lambda_{\min}$).

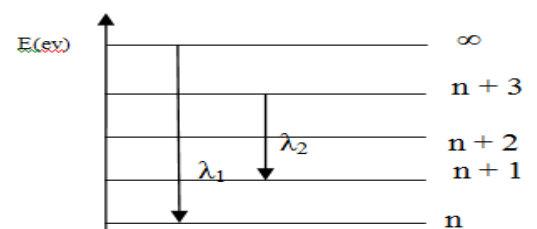
$$\text{We have } \bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \implies \lambda = \frac{1}{R_H} \times \frac{1}{\left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$$

$$\lambda_{\min} = \frac{1}{R_H} \times \frac{1}{\frac{1}{n^2}} \implies \lambda_{\min} = \frac{n^2}{R_H}$$

Exercise

In the emission spectrum of hydrogen, we consider two transitions with respective wavelengths λ_1 and λ_2 , represented in the following graph:

1. Determine the value of n , knowing that $\lambda_1 = 3650\text{\AA}$.
2. Calculate the value of the wavelength λ_2 .
3. To which series of lines do the two transitions



belong?

4. What is the spectral range?

Correction

$$1. \frac{1}{\lambda_1} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_H \left(\frac{1}{n^2} - \frac{1}{\infty^2} \right) \implies \frac{1}{\lambda_1} = \frac{R_H}{n^2} \implies n = \sqrt{R_H \cdot \lambda_1} = 2$$

$$2. \frac{1}{\lambda_2} = R_H \left(\frac{1}{3^2} - \frac{1}{5^2} \right) \quad \lambda_2 = 1,2819 \times 10^{-6} \text{ m} = 1281,9 \text{ nm}$$

$$3. \lambda_1 \implies n_1 = 2 \implies \text{Balmer series} \implies \text{visible region.}$$

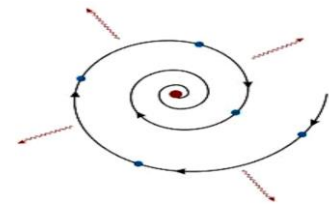
$$\lambda_2 \implies n_1 = 3 \implies \text{Paschen series} \implies \text{IR region.}$$

2.3. Bohr's atomic model: hydrogen atom

This model is a complement to Rutherford's planetary model. The problem with this model is that the electron, an accelerated electric charge, should, according to classical physics, radiate energy and therefore end up crashing into the nucleus. A contradiction exists because the electron does not fall since the atom actually exists.

To resolve the contradiction, Bohr postulated in 1913 that:

- The electron moves in circular orbits placed at well-defined distances from the nucleus.
- During transitions between orbits:
 - ❖ Energy is absorbed (via a photon of energy $h\nu$) if the electron moves away from the nucleus.
 - ❖ Energy is emitted (via a photon of energy $h\nu$) if the electron moves closer to the nucleus.



2.3.1. Bohr's first postulate

The electron in the hydrogen atom moves in a stationary circular orbit (with constant energy) around the nucleus. This electron rotates around the nucleus in a circular orbit of radius r and uniform speed v (**Fig. 2.6**). At any given moment, the electron is subjected to two forces: F_a (attractive electrostatic force) and F_c (centrifugal force).

- F_a : Electrostatic force of attraction which is exerted between the two charges (+e) and (-e).

$$F_a = \frac{-Ke^2}{r^2} \quad \left\{ \begin{array}{l} K = \frac{1}{4\pi\epsilon_0} ; K = 9 \times 10^9 \text{ MKSA} \\ K = 1 \text{ CGS} \\ \epsilon_0 = 8,85 \times 10^{-12} \text{ is the permittivity of vacuum} \end{array} \right.$$

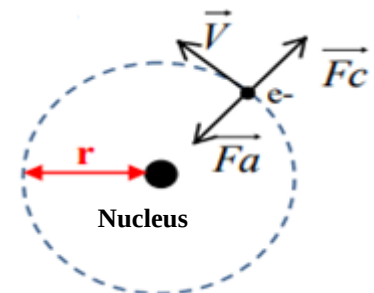


Figure 2.6: The forces exerted on the electron

- F_c : Centrifugal force

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

For the electron to be stable in a circular orbit, it is necessary that:

$$\|\vec{F}_a\| = \|\vec{F}_c\| \implies mv^2 = \frac{Ke^2}{r}$$

m : mass of the electron.

v : speed of the electron.

r : distance e^- - nucleus (radius of the orbit).

e : charge of the electron.

Energy of the electron:

$$E_T = E_k + E_p$$

E_T : total energy

E_k : kinetic energy

E_p : potentielle energy

$$E_k = \frac{1}{2} mv^2 = \frac{Ke^2}{2r}; \quad E_k = \frac{Ke^2}{2r}$$

$$E_p = -\int_{\infty}^r F_a dr = -\int_{\infty}^r -\frac{Ke^2}{r^2} dr = -\frac{Ke^2}{r}; \quad E_p = -\frac{Ke^2}{r}$$

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

2.3.2. Bohr's second postulate

The angular momentum of the system is quantized, it can only take integer multiples of the quantity $\frac{h}{2\pi}$, also known as the quantum unit.

$$mvr = \frac{nh}{2\pi} \implies v = \frac{nh}{2\pi mr}$$

n: a natural number also known as the principal quantum number.

❖ Radius of the hydrogen atom

$$mv^2 = \frac{Ke^2}{r} \implies \frac{mn^2h^2}{4\pi^2m^2r^2} = \frac{Ke^2}{r}$$

$$\implies \frac{n^2h^2}{4\pi^2mr} = Ke^2$$

$$\implies r_n = \frac{n^2h^2}{4\pi^2mKe^2} = a_0 n^2 / a_0 = \frac{h^2}{4\pi^2mKe^2} = 0,529 \times 10^{-10} \text{ m} = 0,529 \text{ \AA}$$

$$a_0 \approx 0,53 \text{ \AA}$$

a_0 : is called the radius of the first Bohr orbit.

$$n = 1 ; r_1 = 0,53 \text{ \AA}$$

$$n = 2 ; 2^{\text{nd}} \text{ Bohr orbit } r_2 = 0,53 \times 2^2 = 2,12 \text{ \AA}$$

$$n = 3 ; 3^{\text{rd}} \text{ Bohr orbit } r_3 = 0,53 \times 3^2 = 4,77 \text{ \AA}$$

❖ The electron speed on a stationary orbit

$$mvr = \frac{nh}{2\pi} \implies v = \frac{nh}{2\pi mr}$$

and

$$r_n = \frac{n^2 h^2}{4\pi^2 m K e^2}$$

$$v = \frac{nh}{2\pi mr} = \frac{nh 4\pi^2 m K e^2}{2\pi m n^2 h^2} = \frac{2\pi k e^2}{nh} ; v_n = \frac{2\pi k e^2}{nh}$$

$$v_1 = \frac{2\pi k e^2}{h} = 2,18 \times 10^6 \text{ m/s}$$

We deduce that : $v_n = \frac{v_1}{n}$

❖ Energy of the hydrogen atom:

We have :

$$\begin{cases} E_T = -\frac{K e^2}{2r} \\ r_n = \frac{n^2 h^2}{4\pi^2 m K e^2} \end{cases} \implies E_n = \frac{-K e^2 4\pi^2 m K e^2}{2 n^2 h^2}$$

$$E_n = \frac{-2\pi^2 m K^2 e^4}{h^2} \times \frac{1}{n^2}$$

$$E_n = \frac{E_1}{n^2} ; E_1 = \frac{-2\pi^2 m K^2 e^4}{h^2} = -21,76 \times 10^{-19} \text{ J} = -13,6 \text{ eV} ; E_n = \frac{-13,6}{n^2} \text{ eV}$$

$$n = 1 ; E_1 = -13,6 \text{ eV}$$

$$n = 2 ; E_2 = -\frac{13,6}{4} \text{ eV}$$

$$n = 3 ; E_3 = -\frac{13,6}{9} \text{ eV}$$

Notes

- When $n = 1$, the atom is in the ground state.
- For $n > 1$, the electron is in an excited state.
- If $n = \infty$, the electron has left the atom, and the atom is said to be ionized.

2.3.3. Bohr's third postulate

The atom emits or absorbs energy only when an electron transitions from one stationary orbit to another (Fig. 2.7):



Figure 2.7 : Absorption and emission.

The energy involved in this process is given by the expression:

$$\Delta E = E_{n_2} - E_{n_1} = \frac{-2\pi^2 m K^2 e^4}{h^2} \times \frac{1}{n_2^2} - \frac{-2\pi^2 m K^2 e^4}{h^2} \times \frac{1}{n_1^2}$$

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

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

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

$$R_H = \frac{2\pi^2 m K^2 e^4}{h^3 c} \quad ; R_H : \text{Rydberg constant}$$

2.4. Application of the Bohr Model to Hydrogen-like ions

Hydrogen-like ions are cations that possess a single electron and Z protons. Examples: He^+ , Li^{2+} , Be^{3+} , ... The general formula for a hydrogen-like ion is: $\frac{A}{Z} X^{(Z-1)+}$

The calculation of the radius and energy of the electron in a hydrogen-like ion for the n -th orbit leads to the following expressions:

$$F_a = \frac{-ZKe^2}{r^2} ; E_p = -\frac{ZKe^2}{r}$$

$$\text{Radius: } r_n (\text{H-like ions}) = \frac{r_n (\text{Hydrogen})}{Z} = a_0 \frac{n^2}{Z} ; r_n = a_0 \frac{n^2}{Z}$$

$$\text{Total energy: } E_n (\text{H-like ions}) = Z^2 E_n (\text{Hydrogen}) ; E_n = \frac{-2\pi^2 m K^2 e^4}{h^2} \times \frac{Z^2}{n^2} ;$$

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

$$\text{Ritz formula: } R_{\text{H-like ions}} = Z^2 R_H$$

2.5. Limitations of the Bohr Model

- ✓ Does not allow explaining certain fine characteristics of the emission spectrum of the hydrogen atom, such as for example the splitting of certain lines under the influence of a magnetic field.

- ✓ It is only valid for hydrogen-like ions (e.g., He^+ , Li^{2+}), not for multi-electron atoms, as it does not account for electron-electron interactions.
- ✓ It cannot describe chemical bonding (particularly covalent bonding), as it oversimplifies electron behavior.

These limitations led to the development of a more advanced model: the quantum mechanical (wave) model of the atom.

2.6. The hydrogen atom in wave mechanics

2.6.1. Wave-particle duality and DeBroglie relation

2.6.1.1. Wave-particle duality of light

Light exhibits a dual nature, both wave-like (wavelength, λ) and particle-like (mass, m).

$$\left. \begin{array}{l} \Delta E = h\nu = \frac{hc}{\lambda} \\ \Delta E = mc^2 \end{array} \right\} \Rightarrow \lambda = \frac{h}{mc}$$

Matter composed of photons (energy $h\nu$) with an apparent mass " m " moves at a speed

$c = 3 \times 10^8$ m/s, exhibiting wave-like behavior with a wavelength $\lambda = \frac{h}{mc}$.

2.6.1.2. Wave-particle duality of matter

De Broglie postulated that matter, like light, possesses a dual nature: wave-like and particle-like. Any moving particle with speed v (particularly electrons) and mass m can be associated with a wave whose wavelength λ is related to its momentum by the following relation:

$$\lambda = \frac{h}{mv} ; \text{ where } h \text{ is Planck's constant.}$$

Note: Wavelength has physical significance only when applied at the microscopic scale (Table 2.2).

Table 2.2: Comparison of wavelengths at microscopic and macroscopic scales.

	Tennis ball	Electron
Mass (m)	200 g	9×10^{-31} g
Speed (v)	30 m/s	3×10^8 m/s
DeBroglie wavelength	$\lambda = 10^{-34}$ m	$\lambda = 2 \times 10^{-10}$ m

2.6.2. Heisenberg's Uncertainty Principle (1927)

Heisenberg's principle states that it is impossible to simultaneously and precisely measure the position x and momentum mv of a particle. It is expressed by the following inequality:

$$\Delta p_x \times \Delta x \geq \frac{h}{2\pi}$$

Δx is the uncertainty in position.

Δp_x is the uncertainty in momentum.

Exercise

An electron is moving in a straight line. Given that its position can be known to within 1 Å, what is the uncertainty in its speed?

$$\Delta x = 1 \text{ Å} = 10^{-10} \text{ m}, m_e = 9,11 \times 10^{-31} \text{ Kg}, \Delta V \geq (h / 2\pi \times m \times \Delta x)$$

$$\Delta V \geq (6,625 \times 10^{-34} / 2\pi \times 9,11 \times 10^{-31} \times 10^{-10}) \Leftrightarrow \Delta V \geq 1,16 \times 10^6 \text{ m/s}$$

The uncertainty in the electron's speed (velocity) is enormous ($\approx 1,16 \times 10^6 \text{ m/s}$). Thus, if we measure the electron's position with a precision of 1 Å, we incur a significant error in measuring its velocity (and vice versa). Similarly, if there is a very large imprecision in the electron's position relative to the nucleus, we transition from the notion of a trajectory to the **concept of a probability domain of presence**, known as an atomic orbital.

2.6.3. Concept of probability of presence

In classical mechanics (Bohr's model), studying the motion of an electron involves precisely determining its trajectory. In contrast, quantum mechanics describes the probability of finding an electron at a specific point in space. This spatial delocalization is represented by a mathematical function of the electron's coordinates, called the **wave function Ψ** . The probability of presence is given by:

$$dP = |\Psi(x,y,z,t)|^2 dV$$

The wave function Ψ must satisfy a specific normalization condition:

$$P = \int |\Psi|^2 dV = 1$$

This ensures the wave function is **normalized**.

2.6.4. Wave Function and Schrödinger's Equation

In 1926, the Austrian physicist Erwin Schrödinger proposed a model in which he described the probability of finding an electron at a given location. This model is known as the electron cloud model or quantum mechanical model. To the classic concept of trajectory, we need to replace it with that of a time-dependent state. The quantum state of a corpuscle such as the electron is characterized by a wave function $\psi(x,y,z)$, which contains all the information it is possible to obtain about the corpuscle.

To study the motion of the electron in the atom, Schrödinger proposed the following equation:

$$\frac{\partial^2 \psi(x,y,z)}{\partial x^2} + \frac{\partial^2 \psi(x,y,z)}{\partial y^2} + \frac{\partial^2 \psi(x,y,z)}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \cdot \psi(x,y,z) = 0$$

$$\Delta \psi(x,y,z) + \frac{8\pi^2 m}{h^2} (E - V) \cdot \psi(x,y,z) = 0 / \Delta = \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$$

Δ : the Laplacian operator

E: total energy of the electron.

V: potential energy of the electron.

m: mass of the electron.

h: Planck's constant.

2.6.5. The resolution of the Schrödinger equation

By solving the Schrödinger equation, which has an infinite number of solutions, we obtain:

- ✓ The analytical expression of $\psi(x,y,z)$, each eigenfunction ψ characterizing a state of the electron called an atomic orbital.
- ✓ Each of these states (atomic orbital) is associated with an eigenvalue of the electron energy described by the corresponding ψ wave function; the expression for the energy is the same as that found by Bohr.
- ✓ For the ψ wave function ((atomic orbital), it involves three numbers called “**quantum numbers**” which characterize the state of an electron. These three numbers are n, l and m.

2.6.6. Quantum numbers and the concept of atomic orbitals

The state of an electron in an atom (its energy and the geometry of the region of space in which it evolves) is defined by the value of 4 parameters called quantum numbers and noted n, l, m, and s.

n: principal quantum number. It characterizes an electron shell, where $n = 1, 2, 3, 4, 5, \dots$ (Table 2.3).

Table 2.3: Different shells

n	1	2	3	4	5	6	7
Layer or shell	K	L	M	N	O	P	Q

l: Secondary or azimuthal quantum number. It characterizes an electron subshell and describes the shape of the orbital, where $0 \leq l \leq n-1$ (Table 2.4).

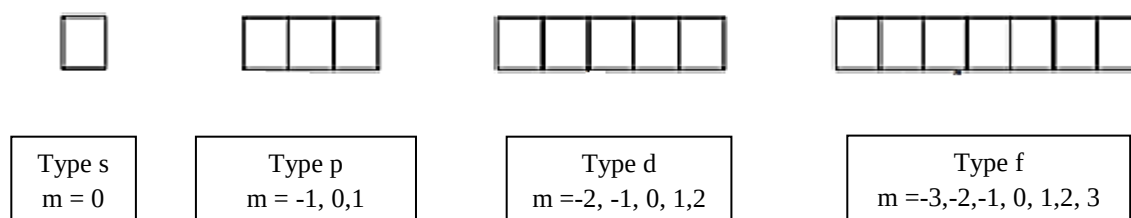
Table 2.4: Different subshells

l	0	1	2	3
Subshell	S	p	d	F

m: Magnetic quantum number; this number defines the number of spatial orientations an electron can adopt when subjected to a magnetic field. It characterizes the quantum box occupied by the electron. The magnetic quantum number m is an integer such that:

$$-l \leq m \leq +l$$

Each orbital can be associated with a quantum box, represented graphically as a square (**Fig. 2.8**).

**Figure 2.8: Atomic orbitals**

s or m_s: Spin quantum number; two possible orientations in an atomic orbital: +1/2 and -1/2.

To symbolize this spin quantum number graphically, we use:

An upward arrow (↑) for $s = +1/2$, with the electron placed on the left in the quantum box;

A downward arrow (↓) for $s = -1/2$, with the electron placed on the right in the quantum box.

The allowed values of l, m, and the maximum number of electrons that a shell can contain are summarized in the following table for the first four shells:

Table 2.5: The allowed values of l , m , and the maximum number of electrons that a shell can contain.

n	l	m	Maximum number of electrons in the shell
1	0	0	2
2	0	0	8
	1	-1, 0, +1	
3	0	0	18
	1	-1, 0, +1	
	2	-2, -1, 0, +1, +2	
4	0	0	32
	1	-1, 0, +1	
	2	-2, -1, 0, +1, +2	
	3	-3, -2, -1, 0, +1, +2, +3	

Notes:

- ✓ An atomic orbital is denoted by $\psi_{n,l,m}$ for example: $\psi_{1,0,0} = 1s$
- ✓ A shell n contains n^2 quantum boxes, and since each quantum box can hold up to 2 electrons, the shell denoted by n could contain $2 n^2$ electrons.

2.7. Poly-electronic atoms in wave mechanics

2.7.1. Electronic configuration of elements

The distribution of electrons among various atomic orbitals is called the electronic configuration of the atom. The filling of these orbitals must strictly adhere to the following rules:

2.7.1.1. Principle of stability statement

In the ground state, electrons in an atom first occupy the most stable atomic orbitals, i.e., those with the lowest energy. The filling of atomic orbitals follows the order: $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$. This order can be easily identified using **Klechkowski's rule (Fig. 2.9)**.

Klechkowski's rule: The filling of energy levels by electrons must occur, in the ground state, in order of increasing values of $(n+l)$. If two levels have the same $(n+l)$ value, the level with the smaller n is filled first.

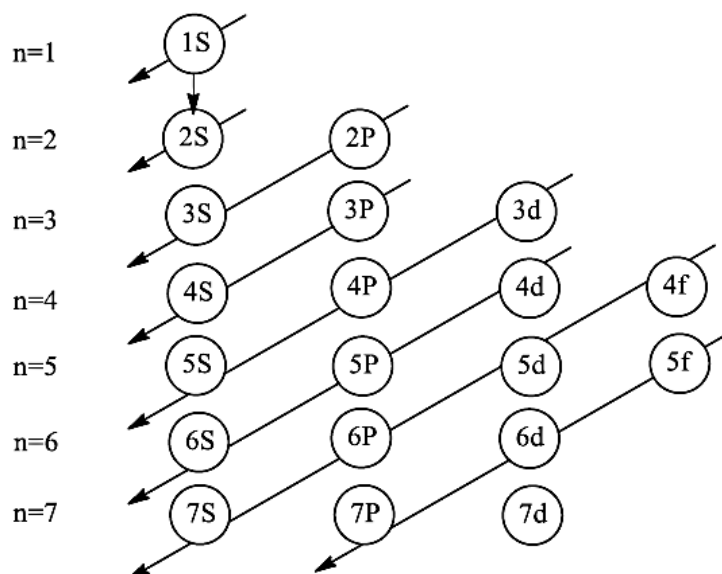
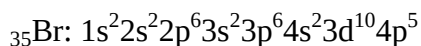
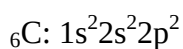
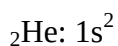
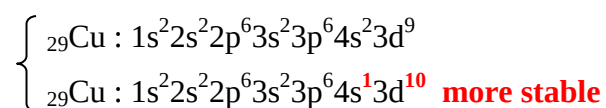
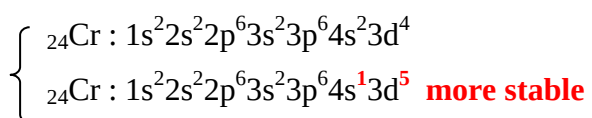


Figure 2.9: Klechkowski's rule.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < \dots$$

Examples**Exception to the Klechkowski rule**

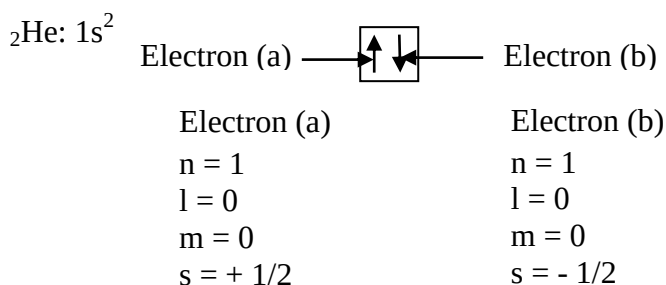
From $n = 4$ onward, the filling of atomic orbitals does not strictly follow the Klechkowski rule. Numerous irregularities appear in the filling of d-subshells.



Note: The "d" subshell is stable when it is half-filled or fully filled.

2.7.1.2. Pauli exclusion principle

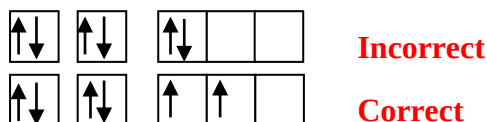
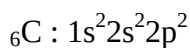
In an atom, two electrons cannot have all their four quantum numbers (n , l , m , and s) identical. For example, in the helium atom, it contains two electrons:



2.7.1.3. Hund's Rule

In the same subshell, electrons tend to occupy the maximum number of quantum boxes with parallel spins.

Example



Abbreviated electron configuration

We can abbreviate the electron configuration of any element by putting brackets around the symbol of the noble gas that occurs just before it on the periodic table and continuing with the valence shell from there.

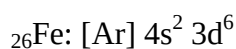
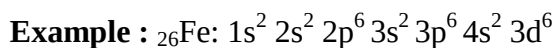
He for $2 < Z < 10$;

Ne for $10 < Z < 18$;

Ar for $18 < Z < 36$;

Kr for $36 < Z < 54$;

Xe for $54 < Z < 86$ and **Rn** for $Z > 86$.



2.7.2. Screen effect: Slater approximation

The Slater approximation (proposed by John C. Slater in 1930) is a semi-empirical method to estimate the effective nuclear charge (Z_{eff}) experienced by an electron in a multi-electron atom. It accounts for the screening effect (or shielding effect), where inner electrons partially shield outer electrons from the full positive charge of the nucleus.

The effective nuclear charge is calculated as:

$$Z_{\text{eff}} = Z - \sum \sigma_{ij}$$

Z: atomic number (total nuclear charge),

σ: screening constant (empirically derived).

With:

σ_{ij}: screening constant for each electron “j” which exerts a screening effect on an electron “i”.

The energy of an electron i in a given atom is given by:

$$E_n = \frac{-13,6}{n^2} Z_{\text{eff}}^2$$

The total energy of the atom is the sum of the contributions from each electron: $E_t = \sum E_i$

According to Slater's proposal, the screening coefficients σ are determined as follows:

Atomic orbitals are separated into several groups:

$$| 1s | 2s, 2p | 3s, 3p | 3d | 4s, 4p | 4d | 4f | 5s, 5p | \dots$$

The screening coefficient σ_i relative to the electron e^- is equal to the sum of the coefficients σ_{ij} due to all electrons other than e.

The following table (**Table 2.6**) gives the values of the coefficients σ_{ij} exerted on the electron “i” by an electron “j”.

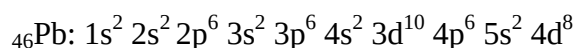
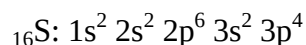
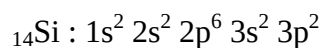
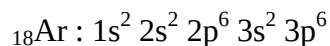
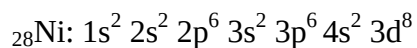
Table 2.6: Screening constant

		e_j							
		1s	2s, 2p	3s, 3p	3d	4s, 4p	4d	4f	5s, 5p
e_i	1s	0,31	0	0	0	0	0	0	0
	2s, 2p	0,85	0,35	0	0	0	0	0	0
	3s, 3p	1	0,85	0,35	0	0	0	0	0
	3d	1	1	1	0,35	0	0	0	0
	4s, 4p	1	1	0,85	0,85	0,35	0	0	0
	4d	1	1	1	1	1	0,35	0	0
	4f	1	1	1	1	1	1	0,35	0
	5s, 5p	1	1	1	1	0,85	0,85	0,85	0,35

Exercise

1. Establish the electron configuration of the following elements: $_{28}\text{Ni}$, $_{18}\text{Ar}$, $_{14}\text{Si}$, $_{16}\text{S}$, $_{82}\text{Pb}$
2. Calculate the Z_{eff} (effective nuclear charge) for each element.
3. For each element, calculate the orbital radius of the electron in the outermost shell.

4. Calculate the energy (in eV and joules) of the electron in the outermost shell for each element.

Correction**1. The electron configuration of the elements****2. Calculation of Z_{eff}**

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

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

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

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

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

3. Calculation of atomic radius

$$r_a = \frac{0,53n^2}{Z_{\text{eff}}} \text{ (\AA)}$$

$${}_{28}\text{Ni}: n = 4 \quad Z_{\text{eff}} = 4,05 \quad r_a = 2,09 \text{ \AA}$$

$${}_{18}\text{Ar}: n = 3 \quad Z_{\text{eff}} = 6,75 \quad r_a = 0,706 \text{ \AA}$$

$${}_{14}\text{Si}: n = 3 \quad Z_{\text{eff}} = 4,15 \quad r_a = 1,15 \text{ \AA}$$

$${}_{16}\text{S}: n = 3 \quad Z_{\text{eff}} = 5,45 \quad r_a = 0,875 \text{ \AA}$$

$${}_{46}\text{Pb}: n = 5 \quad Z_{\text{eff}} = 4,05 \quad r_a = 3,27 \text{ \AA}$$

4. Calculation of the energy of the electron located in the outermost shell

$$E_n = \frac{-13,6}{n^2} Z_{\text{eff}}^2$$

$${}_{28}\text{Ni}: n = 4 \quad Z_{\text{eff}} = 4,05 \quad E_n = -13,94 \text{ eV} \quad E_n = -22,3 \times 10^{-19} \text{ Joules}$$

$${}_{18}\text{Ar}: n = 3 \quad Z_{\text{eff}} = 6,75 \quad E_n = -68,85 \text{ eV} \quad E_n = -110,16 \times 10^{-19} \text{ Joules}$$

$${}_{14}\text{Si}: n = 3 \quad Z_{\text{eff}} = 4,15 \quad E_n = -26,02 \text{ eV} \quad E_n = -41,64 \times 10^{-19} \text{ Joules}$$

$${}_{16}\text{S}: n = 3 \quad Z_{\text{eff}} = 5,45 \quad E_n = -44,88 \text{ eV} \quad E_n = -71,8 \times 10^{-19} \text{ Joules}$$

$${}_{46}\text{Pb}: n = 5 \quad Z_{\text{eff}} = 4,05 \quad E_n = -8,92 \text{ eV} \quad E_n = -14,27 \times 10^{-19} \text{ Joules}$$

Exercises

Exercise 1

1. According to the Bohr model, give the expression for E_n , the total energy of the electron in the hydrogen atom at energy level n .
2. Express E_n in terms of E_1 , the energy of the hydrogen atom in its ground state.
3. Calculate E_n for the energy levels $n=1,2,3,4$, and ∞ for Hydrogen.
4. Calculate the energy absorbed by Hydrogen atom to transition from the ground state to the 1st excited state, 2nd excited state, and the ionized state. If this energy is in the form of light, calculate the corresponding wavelengths.

Exercise 2

1. Consider a hydrogen atom in its excited state n_2 . During de-excitation, it emits two photons with wavelengths $\lambda_1 = 406.1$ nm and λ_2 .
2. Determine the corresponding transitions
3. Calculate λ_2 and the energy corresponding to this transition.
4. The return from state n_2 to the ground state can occur in a single step (emission of a single photon of wavelength λ_3). Give the relationship between λ_1 , λ_2 , and λ_3 . Deduce λ_3 .

Exercise 3

The electron of a hydrogen atom in the energy state $E_n = -0.85$ eV undergoes a transition to the energy level $E_{n'} = -3.44$ eV.

1. Calculate the energy and wavelength of the emitted photon.
2. Which transition does this emission correspond to?
3. Give the relationship between the wavelengths λ_z and λ_H of the radiation emitted by a hydrogen-like ion and the hydrogen atom, respectively, during the same transition.
4. Calculate the wavelength corresponding to the same transition for the hydrogen-like ion ${}^4_ZX^{3+}$

Exercise 4

During the transition of the electron of a hydrogen-like ion ${}_ZX^{b+}$ from the 6th excited state to the 4th excited state, a light radiation of frequency $\nu = 2,57.10^{14}$ S⁻¹ is emitted.

1. Determine Z and deduce b .
2. For the same transition, calculate the wavelength λ_H for the hydrogen atom. To which series of lines does it belong?

3. Calculate the wavelength of the 1st line ($\lambda_{\max}$) and the final line ($\lambda_{\min}$) of this series for hydrogen.
4. Calculate the energies in eV corresponding to the three transitions (λ_H , $\lambda_{\max}$, $\lambda_{\min}$).

Data: $1\text{eV}=1,6.10^{-19}\text{ J}$, $h = 6,62.10^{-34}\text{J.s}$, $R_H = 1,1.10^7\text{ m}^{-1}$, $C = 3.10^8\text{ m/s}$, $1\text{m} = 10^{10}\text{ \AA}=10^9\text{ nm}$, $a_0 = 0.53\text{ \AA}$.

Correction

Exercise 1

1. Expression for E_n according to the Bohr model

The total energy of the electron in the hydrogen atom at energy level n is given by:

$$E_n = \frac{-2\pi^2 m K^2 e^4}{h^2} \times \frac{1}{n^2}$$

2. Expression for E_n in terms of E_1

$$E_1 = \frac{-2 \times (3,14)^2 \times 9,1 \times 10^{-31} \times (9 \times 10^9)^2 \times (1,6 \times 10^{-19})^4}{(6,62 \times 10^{-34})^2} \times \frac{1}{1^2} = -21,76 \times 10^{-19} \text{ J} = -13,6 \text{ eV}.$$

$$\text{So ; } E_n = \frac{E_1}{n^2} = \frac{-13,6}{n^2} \text{ eV}$$

3. Calculation of E_n for $n = 1, 2, 3, 4, \infty$

$$n=1 \longrightarrow E_1 = -13,6 \text{ eV}$$

$$n=2 \longrightarrow E_2 = -\frac{13,6}{4} \text{ eV} = -3,4 \text{ eV}$$

$$n=3 \longrightarrow E_3 = -\frac{13,6}{9} \text{ eV} = -1,51 \text{ eV}$$

$$n=4 \longrightarrow E_4 = -\frac{13,6}{16} \text{ eV} = -0,85 \text{ eV}$$

$$n=\infty \longrightarrow E_\infty = -\frac{13,6}{\infty} \text{ eV} = 0 \text{ eV}$$

4. Energy absorbed and corresponding wavelengths for transitions from ground state to 1st excited state, 2nd excited state, and the ionized state.

Energy absorbed for transitions from ground state ($n=1$) to a higher state n is:

$$\Delta E_{1 \rightarrow n} = E_n - E_1 = 13,6 \left(1 - \frac{1}{n^2}\right)$$

The wavelength λ of light corresponding to this energy is given by:

$$\lambda = \frac{hc}{\Delta E}$$

Transition to 1st excited state ($n=2$):

$$\Delta E = 13,6 \left(1 - \frac{1}{2^2}\right) = 10,2 \text{ eV}$$

$$\lambda \approx 121,6 \text{ nm}$$

Transition to 2nd excited state ($n=3$):

$$\Delta E = 13,6 \left(1 - \frac{1}{3^2}\right) = 12,09 \text{ eV}$$

$$\lambda \approx 102,6 \text{ nm}$$

Transition to ionized state ($n=\infty$):

$$\Delta E = 13,6 (1 - 0) = 13,6 \text{ eV}$$

$$\lambda \approx 91,2 \text{ nm}$$

Exercise 2

1. Transitions identification

The hydrogen atom is initially in the excited state n_2

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

$$\lambda_1 = 406,1 \text{ nm} \in \text{visible} \longrightarrow n_1 = 2$$

$$n_2 = 6$$

Transition $6 \longrightarrow 2$

$$\Delta E_{6 \rightarrow 2} = \frac{-h \times c}{\lambda_{6 \rightarrow 2}} = -3,03 \text{ eV}$$

λ_2 corresponds to the $2 \longrightarrow 1$ transition

2. Calculation of λ_2 and its Energy

$$\frac{1}{\lambda_2} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_H \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \longrightarrow \lambda_2 = \frac{1}{R_H \left(\frac{1}{1^2} - \frac{1}{2^2} \right)} = 1210 \text{ \AA}$$

$$\Delta E_{2 \rightarrow 1} = E_1 - E_2 = -13,6 - (-3,4) = -10,2 \text{ eV}$$

3. Relationship between λ_1 , λ_2 , and λ_3 and deduction of λ_3

$$\Delta E_3 = \Delta E_1 + \Delta E_2 \longrightarrow \frac{hc}{\lambda_3} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2} \longrightarrow \frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda_3 = 93,5 \text{ nm}$$

Exercise 3

1. Energy and wavelength of the emitted photon

$$\Delta E_{n \rightarrow n'} = E_{n'} - E_n = -3,44 + 0,85 = -2,59 \text{ eV}$$

$$\Delta E = \frac{hc}{\lambda} \longrightarrow \lambda = \frac{hc}{\Delta E} = \frac{6,62 \times 10^{-34} \times 3 \times 10^8}{2,59 \times 1,6 \times 10^{-19}} = 4,79 \times 10^{-7} \text{ m}$$

2. Identification of the transition

$$E_n = \frac{-13,6}{n^2} \longrightarrow n = \sqrt{\frac{-13,6}{E_n}} = \sqrt{\frac{-13,6}{-0,85}} = 4$$

$$E_{n'} = \frac{-13,6}{n'^2} \longrightarrow n' = \sqrt{\frac{-13,6}{E_{n'}}} = \sqrt{\frac{-13,6}{-3,44}} = 2$$

Thus, the transition is from $n=4$ to $n=2$, which corresponds to the second line of the Balmer series.

3. Relationship between wavelengths λ_Z and λ_H

$$\left. \begin{aligned} \frac{1}{\lambda_H} &= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ \frac{1}{\lambda_Z} &= R_H \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \end{aligned} \right\} \longrightarrow \frac{1}{\lambda_Z} = \frac{Z^2}{\lambda_H} \longrightarrow \begin{aligned} \lambda_H &= Z^2 \times \lambda_Z \\ \lambda_Z &= \frac{\lambda_H}{Z^2} \end{aligned}$$

4. Wavelength for the Hydrogen-like ion ${}_4X^{3+}$

$$\lambda_Z = \frac{4,79 \times 10^{-7}}{5^2} = 0,1916 \times 10^{-7} \text{ m}$$

Exercise 4

1. Determine Z and deduce b

6th excited state: $n = 7$

4th excited state: $n = 5$

So, the transition is from $n_2 = 7$ to $n_1 = 5$

$$\nu = \frac{c}{\lambda} = C \times R_H \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \longrightarrow Z = \sqrt{\frac{\nu}{C \times R_H \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}} = 2, b = 1$$

2. Wavelength λ_H for hydrogen and series identification for hydrogen ($Z=1$), the same transition ($n_2=7 \rightarrow n_1=5$):

$$\frac{1}{\lambda_H} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \longrightarrow \lambda_H = 4640 \text{ nm}$$

The transition identified ($n=7 \rightarrow n=5$) is consistent with the **Pfund** series in hydrogen.

3. First line ($\lambda_{\max}$) and final line ($\lambda_{\min}$) of the Pfund series

First line: transition from $n_2=6$ to $n_1=5$

$$\lambda_{\max} = \lambda_{6 \rightarrow 5} = 7458,79 \text{ nm}$$

Final line: transition from $n_2 = \infty$ to $n_1=5$

$$\lambda_{\min} = \lambda_{\infty \rightarrow 5} = 2278,94 \text{ nm}$$

4. Energies in eV for the three transitions

$$\Delta E = \frac{-hc}{\lambda}$$

$$\Delta E_H = \Delta E_{7 \rightarrow 5} = -0,27 \text{ eV}$$

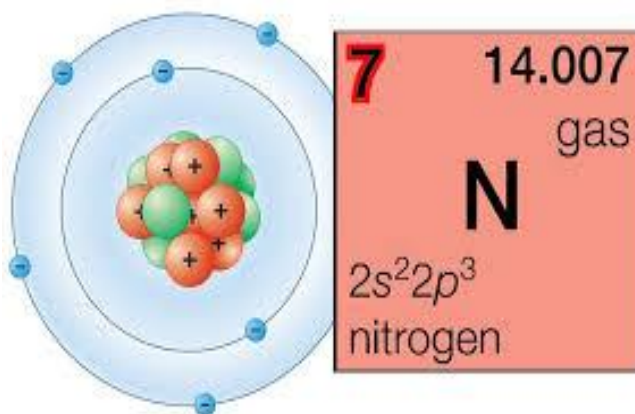
$$\Delta E_{\min} = \Delta E_{6 \rightarrow 5} = -0,166 \text{ eV}$$

$$\Delta E_{\max} = \Delta E_{\infty \rightarrow 5} = -0,544 \text{ eV}$$



Chapter 3

Periodic classification of the elements



Chapter 3

Periodic classification of the elements

3.1. Development of the periodic table

The Periodic table is a tabular arrangement of the chemical elements, organized by their atomic number, electron configuration, and recurring chemical properties. Its development was not the work of a single person but a gradual process over a century.

Before a table could be built, elements had to be identified and a key organizing principle (atomic weight) had to be established.

3.1.1. Early foundations and precursors

- **Antoine Lavoisier (1789):** Compiled the first modern list of 33 chemical elements, distinguishing between elements and compounds.
- **Jöns Jakob Berzelius (1828):** Developed a system of chemical symbols and, crucially, worked to accurately measure the **atomic weights** of many elements, providing essential data for future classification.
- **Johann Döbereiner (1817-1829):** Noticed groups of three elements with similar properties, which he called "**Triads**." The atomic weight of the middle element was roughly the average of the other two (e.g., Cl, Br, I; Ca, Sr, Ba). This was the first hint of a relationship between atomic weight and chemical properties.

As more elements were discovered, scientists began to see patterns when they arranged them by increasing atomic weight.

3.1.2. The first periodic laws and tables

- **John Newlands (1864):** An English chemist who arranged the known elements in order of atomic weight and proposed the "**Law of Octaves**." He observed that every eighth element had similar properties, like notes in a musical scale. While a step forward, his law broke down after calcium and was ridiculed by his contemporaries.
- **Lothar Meyer (1868) & Dmitri Mendeleev (1869):** Working independently, both the Russian Mendeleev and the German Meyer produced remarkably similar periodic tables based on the **periodic recurrence of properties** when elements were arranged by atomic weight.

- **Mendeleev's Genius:** His version was published first and was far more influential because of two critical decisions:
 - ✓ **He left gaps:** He boldly left empty spaces in his table for elements he predicted must exist but had not yet been discovered (e.g., "eka-aluminum," "eka-silicon").
 - ✓ **He swapped elements:** When the order by atomic weight contradicted the chemical properties, he prioritized the properties. For example, he placed tellurium before iodine, even though its atomic weight was slightly higher, because tellurium's properties matched those of oxygen and sulfur.

Mendeleev's predictions for the missing elements (gallium, scandium, germanium) were so accurate that his table was widely accepted.

3.1.3. The modern foundation: From atomic weight to atomic number

Mendeleev's table had a few remaining inconsistencies (the "tellurium-iodine" problem). The solution came from a new understanding of the atom.

- ✓ **Henry Moseley (1913):** Using X-ray spectroscopy, this English physicist discovered that the fundamental property for ordering the elements was not atomic weight, but **atomic number (Z)**, which represents the number of protons in the nucleus.
- ✓ **Glenn Seaborg (1940-1950):** While working on the Manhattan project, the American chemist discovered the actinide series (elements 89-103). He realized these elements were part of a new f-block series, and he famously "reorganized" the periodic table by moving them out of the main body and placing them below the lanthanides. This is the form of the table we use today.

The modern periodic classification is characterized by the arrangement of elements in order of increasing atomic number. The table is structured into horizontal rows called **periods** and vertical columns known as **groups**. There are seven periods, numbered 1 through 7, and 18 groups. A key principle of this classification is that elements within the same group possess the same number of electrons in their outermost shell, which is the fundamental reason for their similar chemical properties.

3.2. Description of the periodic table

3.2.1. Periods (Rows)

The period corresponds to an electronic shell identified by its principal quantum number noted (n). There are seven 7 periods numbered from $n = 1$ to $n = 7$ or noted shells K, L, M...

The period is given by the highest principal quantum number appearing in the electronic configuration.

Example

${}_6\text{C} : 1s^2 2s^2 2p^2 \rightarrow$ The period of Na is : 2.

${}_{35}\text{Br} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5 \rightarrow$ The period of Br is: 4.

3.2.2. Groups (Columns)

Elements in the same column (group) having the same electronic configuration of the outer shell. There are 18 groups, 8 of which are in subgroup A and 10 in subgroup B (**Table 3.1**).

The group is indicated by a Roman numeral and designated by the number of electrons located in the last shell (or valence shell); except groups VIII_B, I_B and II_B.

I(1), II(2), III(3), IV(4), V(5), VI(6), VII(7), VIII(8), IX(9), X(10)

3.2.3. Subgroups

The groups of the periodic table are divided into two subgroups: subgroup **A** and **B**.

Subgroup A: the valence electrons occupy the s or p orbitals, i.e. the s block or the p block,

Subgroup B: the electrons of the d subshell act as valence electrons, i.e. the d block.

Examples

${}_{19}\text{K} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, a single valence electron $\rightarrow$ K belongs to group **I_A**.

${}_{18}\text{Ar} : 1s^2 2s^2 2p^6 3s^2 3p^6$, 8 valence electrons $\rightarrow$ Kr belongs to group **VIII_A**.

${}_{21}\text{Sc} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$, 3 valence electrons $\rightarrow$ Sc belongs to group **III_B**.

Table 3.1: Different groups in periodic table.

Valence structure	ns^1	ns^2	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$	$ns^1 (n-1)d^{10}$
Group	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	VIII_A	I_B
Number of valence electrons	1	2	3	4	5	6	7	8	1

Valence structure	$ns^2 (n-1)d^{10}$	$ns^2 (n-1)d^1$	$ns^2 (n-1)d^2$	$ns^2 (n-1)d^3$	$ns^2 (n-1)d^4$	$ns^2 (n-1)d^5$
Group	II_B	III_B	IV_B	V_B	VI_B	VII_B
Number of valence electrons	2	3	4	5	6	7

Valence structure	$ns^2 (n-1)d^6, ns^2 (n-1)d^7, ns^2 (n-1)d^8$
Group	VIII_B
Number of valence electrons	8

3.2.4. Blocks

The periodic table is divided into blocks based on the type of atomic orbital that is being filled with electrons in the elements of that region. This classification is fundamental to understanding the electron configuration and, consequently, the chemical properties of elements. There are four main blocks: **s-block**, **p-block**, **d-block**, and **f-block** (Fig 3.1).

- The **s-block** corresponds to columns 1 and 2: elements in ns^1 and ns^2 configurations.
- The **d-block** has 10 columns, from 3 to 12: progressive filling of the $(n - 1) d$ subshell, with the ns subshell being saturated at ns^2 .
- The **p-block** corresponds to columns 13 to 18: progressive filling of the np subshell, with the $(n - 1) d$ and ns subshells being saturated at $(n - 1) d^{10}$ and ns^2 .
- The **f-block** contains two families: filling of the $(n-2) f$ subshells.

In the case of Helium, although belonging to the s-block, it is placed in the p-block (noble gases group).

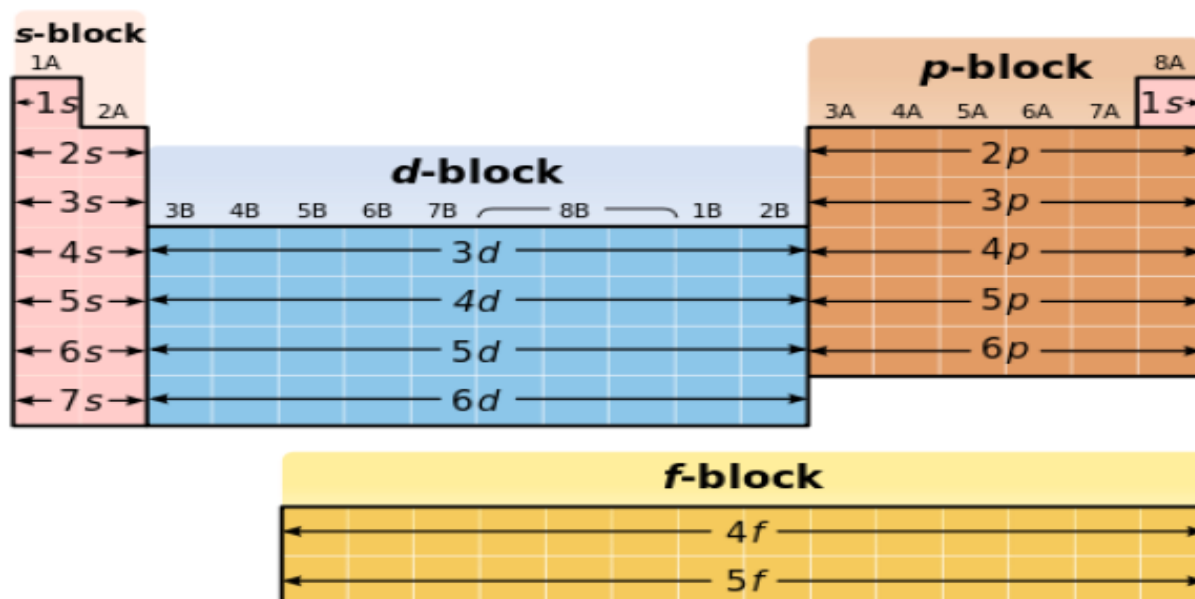


Figure 3.1: The blocks of periodic table.

3.2.5. Families

The main families of the periodic table (Fig. 3.2):

- **Alkali metals** (column 1): group **I_A**: electronic configuration: ns^1 . (Li, Na, K, Rb, Cs). All the elements in this column have an outer layer with an electron. They all form cations by losing an electron

PERIODIC TABLE OF ELEMENTS

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18																			
1	1 H Hydrogen 1.008	Atomic # Symbol Name Weight																2 He Helium 4.0026	
	3 Li Lithium 6.94	4 Be Beryllium 9.0122															10 Ne Neon 20.180		
	11 Na Sodium 22.990	12 Mg Magnesium 24.305															18 Ar Argon 39.948		
2	C Solid Hg Liquid H Gas Rf Unknown																		
	Metals Alkali metals Alkaline earth metals Lanthanoids (Lanthanides) Actinoids (Actinides) Transition metals Post-transition metals Metalloids Nonmetals Other nonmetals Noble gases																		
3	5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180													18 Ar Argon 39.948
	13 Al Aluminium 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948													
4	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798	
	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29	
	55 Cs Caesium 132.91	56 Ba Barium 137.33	57–71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)	
	87 Fr Francium (223)	88 Ra Radium (226)	89–103	104 Rf Rutherfordium (267)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (277)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (290)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)	
5	For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.																		
6	57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.05	71 Lu Lutetium 174.97				
	89 Ac Actinium (227)	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (266)				
7	Design Copyright © 2017 Michael Dayah (michael@dayah.com). For a fully interactive version with orbitals, isotopes, compounds, and free printouts, visit http://www.ptable.com/																		

Figure 3.2: Periodic table.

- **Alkaline earth metals** (column 2): group **II_A**, electronic configuration **ns²** (Be, Mg, Ca, Sr, Ba, Ra). All have two electrons on their outer layer. They all form cations by losing two electrons.
- **Halogens** (column 17): group **VII_A**: electronic configuration **ns²np⁵** (F, Cl, Br, I, At).
- **Rare (noble or inert) gases** (column 18): group **VIII_A**: electronic configuration **ns²np⁶** (He, Ne, Ar, Kr, Xe, Rn).
- **Non-metals** (column 13 to 16): groups: (**III_A**; **IV_A**; **V_A**; **VI_A**)
- **Transition metals** (column 3 to 12): groups: (**III_B**; **IV_B**; **V_B**; **VI_B**; **VII_B**; **VIII_B**, **I_B**; **II_B**), these are elements which have incompletely filled (d) orbitals
- **Rare earths (Internal transition metals)**, the elements have the orbitals (f) in the process of being filled, in fact the orbitals which correspond to the filling of the 4f orbital are called the **Lanthanides** (6th period: elements from Z=57 to Z=71), those which correspond to the filling of the 5f orbital are called the **Actinides** (7th periods: elements from Z=89 to Z=103).

3.3. Evolution and periodicity of the physicochemical properties of elements

The chemical properties of an element depend essentially on the electronic configuration of the valence shell. Being the most energetic, it therefore contains the most reactive electrons.

3.3.1. Atomic radius (r)

The atomic radius is defined as one-half the distance between the centers of two adjacent atoms (**Fig. 3.3**).

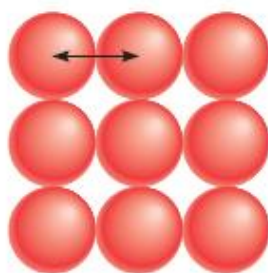


Figure 3.3: Atomic radius.

Across a period (left to right): The atomic radius decreases. This is because the number of protons in the nucleus increases, creating a stronger positive charge that pulls the electrons closer to the nucleus (**Fig. 3.4**).

Down a group: The atomic radius increases. This is because each new period adds an electron shell, which is further from the nucleus. While the nuclear charge also increases, the effect of the added shells and increased distance outweighs the increased attraction, leading to a larger radius.

- Over a period: if Z increases then r_a decreases.
- Over a column: if Z increases then r_a increases.

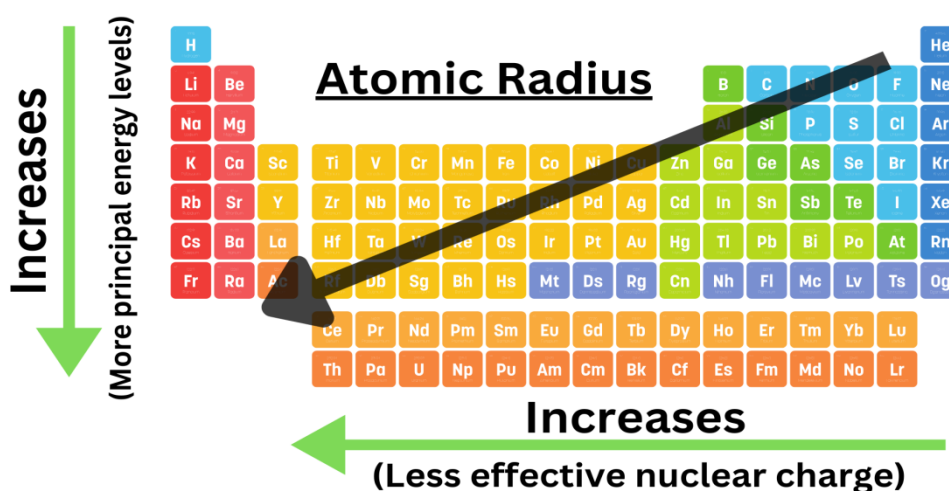


Figure 3.4: Variation of atomic radius.

Ionic radius

A cation is positively charged: $r_{\text{cation}} < r_{\text{atom}}$

$$r(\text{Ca}^{+2}) < r(\text{Ca})$$

$$r_{\text{Li}} : 0,123 \text{ nm} \quad r_{\text{Li}^+} : 0,060 \text{ nm}$$

$$r_{\text{Al}} : 0,125 \text{ nm} \quad r_{\text{Al}^{3+}} : 0,005 \text{ nm}$$

An anion is negatively charged so: $r_{\text{Anion}} > r_{\text{atom}}$

$$r(\text{Cl}^-) > r(\text{Cl})$$

$$r_{\text{S}} : 0,104 \text{ nm} \quad r_{\text{S}^{2-}} : 0,184 \text{ nm}$$

A comparison of atomic radius with ionic radius is represented in the **Fig. 3.5**.

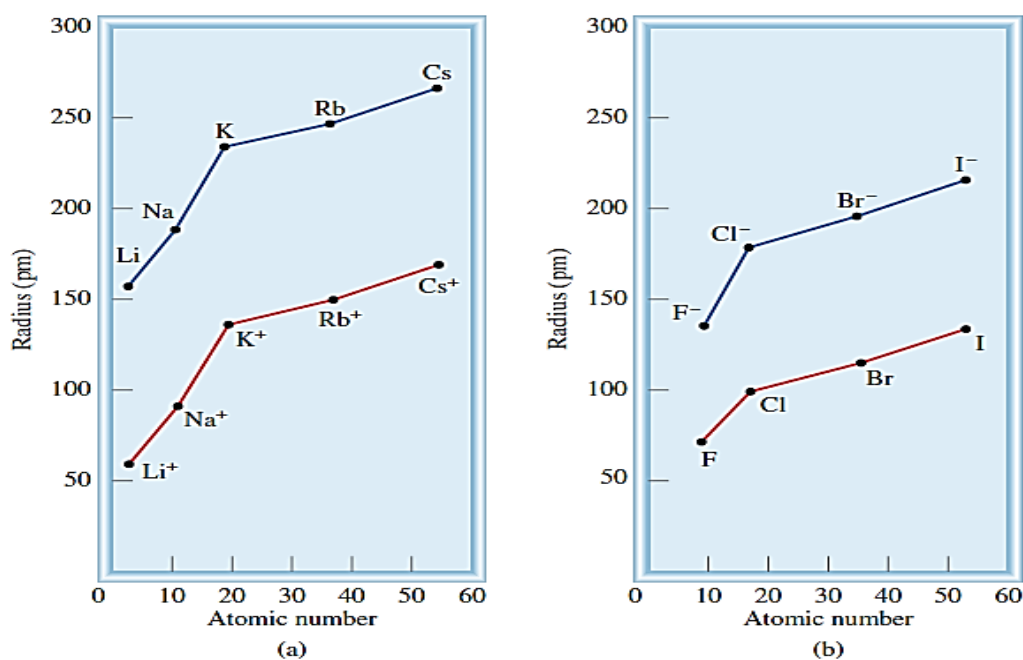


Figure 3.5: Comparison of atomic radius with ionic radius. (a) Alkali metals and alkali metal cations. (b) Halogens and halide ions.

3.3.2. Ionization energy (IE)

Ionization energy, denoted (IE), also called ionization potential, is the energy required to remove an electron from an atom in its gaseous state.

The equation for ionization energy is:



Across a period (left to right): Ionization energy generally increases. This is because the number of protons in the nucleus increases, leading to a stronger positive charge that pulls electrons more tightly.

Down a group (top to bottom): Ionization energy generally decreases. As you move down a group, the outermost electrons are in higher energy shells and are shielded from the nucleus by more inner electrons, making them easier to remove (**Fig. 3.6**).

- Over the same period: if Z increases then IE increases.
- Over the same group: if Z increases then IE decreases.

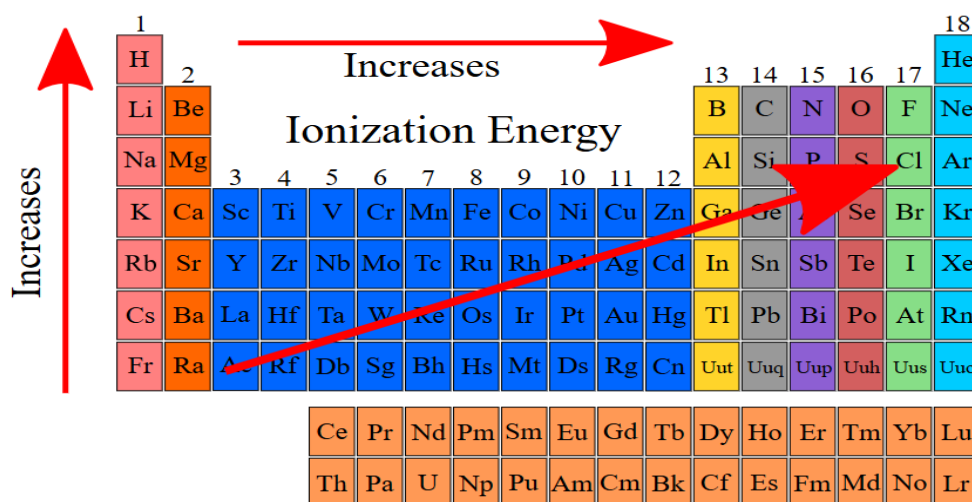
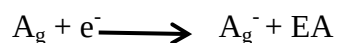


Figure 3.6: Variation of ionization energy.

3.3.3. Electron affinity

Electron affinity is the amount of energy released when an electron is added to a neutral atom to form an anion, according to the reaction:



The variation in electron affinity is broadly similar to that of ionization energy. Thus: electron affinity increases from left to right along the periods of the classification, and decreases along the columns (Fig. 3.7).

- Over the same period: if Z increases then AE increases.
- Over the same group: if Z increases then AE decreases.

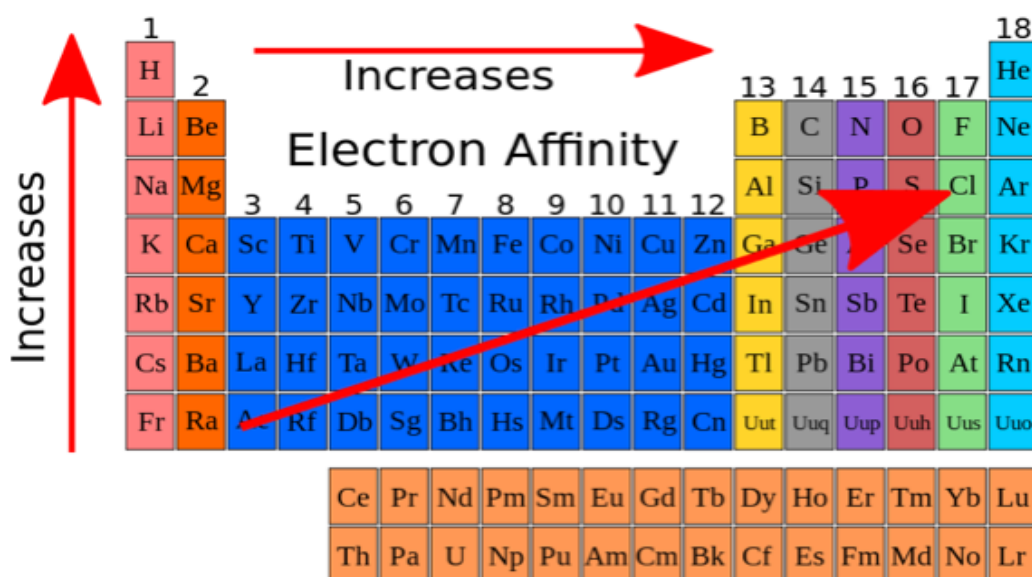


Figure 3.7 : Variation of electron affinity.

3.3.4. Electronegativity (χ)

It is a measure that characterizes an atom's ability to attract electrons towards itself when forming a chemical bond with another element; it is a relative measure.

$A_g + B_g \longrightarrow A_g^+ + B_g^-$, it is said that B is more electronegative than A.

Moving left to right across a period increases electronegativity. As you move left to right, the amount of protons increases, while the amount of core electrons remains the same. This means that effective nuclear charge increases. Bonding electrons experience a stronger attraction to the nucleus, indicating increased electronegativity.

Moving down a group decreases electronegativity. Moving down a group adds more energy levels. The valence electrons, which participate in bonds, are further from the nucleus. There will also be more core electrons, so the bonding valence electrons experience a greater shielding effect. The bonding electrons are less attracted to the nucleus, so electronegativity has decreased.

Note that we assign noble gases electronegativities of zero because they do not typically form bonds.

- Within the same period: as Z increases, χ increases.
- Within the same group: as Z increases, χ decreases (**Fig. 3.8**).

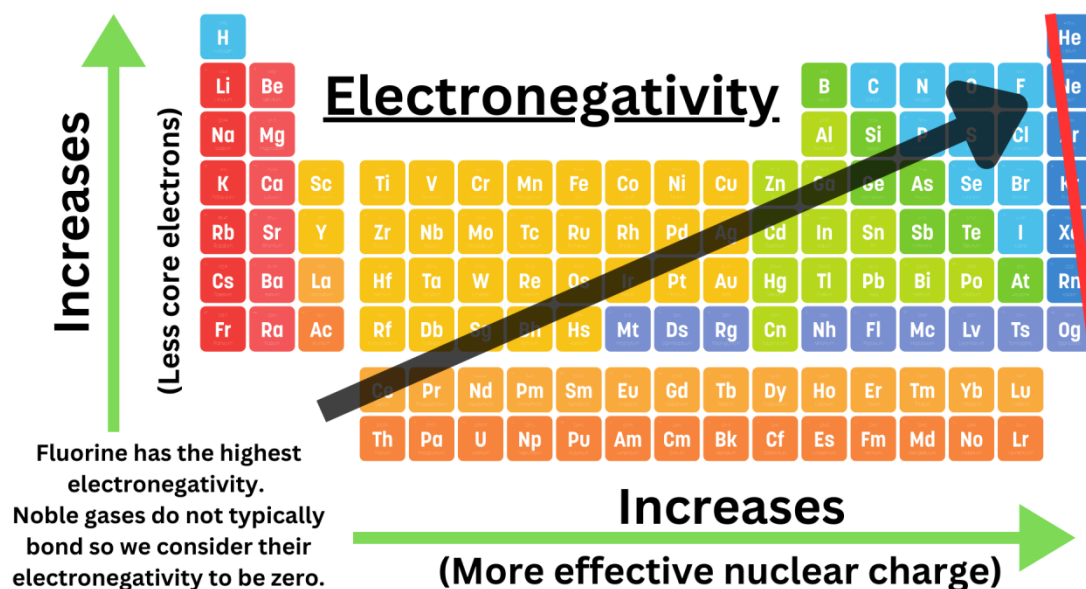


Figure 3.8 : Variation of electronegativity.

The electronegativity of an element X can be defined according to several scales:

a. Mulliken scale

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

$$\chi = \frac{EA + IE}{2}$$

EA is the electron affinity;

IE is the first ionization energy.

b. Pauling scale: the difference in electronegativity between elements A and B is expressed as:

$$\Delta = |\chi_A - \chi_B| = 0,102 \sqrt{E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}}}$$

Where:

E_{A-B} , E_{A-A} , and E_{B-B} are the binding energies (in KJ/mol) of the diatomic molecules A-B, A-A, and B-B, respectively

Exercise

I) Consider the elements: ${}^{58}_{28}\text{Ni}$; ${}^{31}_{15}\text{P}$; ${}^{35}_{17}\text{Cl}$; ${}^{65}_{30}\text{Zn}$

- 1) Give the electronic structures of these elements.
- 2) Identify the positions of these elements in the periodic table (period, group, and block).
- 3) Which element is the most electronegative?

II) Give the electronic configurations of the three elements X, Y and Z knowing that:

- 1) X^{3+} has the structure of neon (${}_{10}\text{Ne}$).
- 2) Y belongs to the same period as X and is missing two electrons from Y to have the configuration of a noble gas.
- 3) Z^+ has the structure of the noble gas which belongs to the period of Y.

Correction

Element	Electronic configuration	Period	Group	Block
${}^{58}_{28}\text{Ni}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ [Ar] $4s^2 3d^8$	4	VIII _B	d
${}^{31}_{15}\text{P}$	$1s^2 2s^2 2p^6 3s^2 3p^3$ [Ne] $3s^2 3p^3$	3	V _A	p
${}^{35}_{17}\text{Cl}$	$1s^2 2s^2 2p^6 3s^2 3p^5$ [Ne] $3s^2 3p^5$	3	VII _A	p
${}^{65}_{30}\text{Zn}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ [Ar] $4s^2 3d^{10}$	4	II _B	d

3. Chlorine (Cl) is the most electronegative element in this list.

II) 1. X^{3+} has the structure of neon ($_{10}\text{Ne}$).

The electron configuration of Neon (Ne) is $1s^2 2s^2 2p^6$.

X^{3+} is an ion that has lost 3 electrons and now has this configuration. Therefore, the neutral atom X must have 3 more electrons than Ne.

Number of electrons in neutral X = 10 (from Ne) + 3 = 13.

The element with atomic number $Z = 13$ is Aluminum (Al).

Configuration of X (Al): $1s^2 2s^2 2p^6 3s^2 3p^1 \rightarrow [\text{Ne}] 3s^2 3p^1$

Configuration of X^{3+} (Al^{3+}): $1s^2 2s^2 2p^6 \rightarrow$ same as Ne.

2. Y belongs to the same period as X and is missing two electrons from Y to have the configuration of a noble gas.

X is Aluminum (Al), which is in Period 3.

Therefore, Y is also in Period 3.

The noble gas at the end of Period 3 is Argon (Ar), with the configuration $[\text{Ne}] 3s^2 3p^6$ (18 electrons).

Y is missing 2 electrons to have this stable configuration. This means the neutral atom Y has 2 electrons less than Argon.

Number of electrons in neutral Y = 18 (from Ar) - 2 = 16.

The element with atomic number $Z = 16$ is Sulfur (S).

Configuration of Y (S): $1s^2 2s^2 2p^6 3s^2 3p^4 \rightarrow [\text{Ne}] 3s^2 3p^4$. It needs 2 more electrons to complete its p subshell and become $[\text{Ne}] 3s^2 3p^6$ (Ar).

3. Z^+ has the structure of the noble gas which belongs to the period of Y.

Y is Sulfur (S), which is in Period 3.

The noble gas for Period 3 is Argon (Ar), with the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$.

Z^+ is an ion that has lost 1 electron and now has the same configuration as Argon.

Therefore, the neutral atom Z must have had 1 more electron than Ar.

Number of electrons in neutral Z = 18 (from Ar) + 1 = 19.

The element with atomic number $Z = 19$ is Potassium (K).

Configuration of Z (K): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 \rightarrow [\text{Ar}] 4s^1$

Configuration of Z^+ (K^+): $1s^2 2s^2 2p^6 3s^2 3p^6 \rightarrow$ same as Ar.

Exercises

Exercise 1

Can the quantum numbers n , l , and m together have the following values? If yes, what subshell do they characterize?

	a	b	c	d	e	f	g	h	i	j
n	2	4	3	4	2	5	4	2	3	5
l	0	1	1	-1	0	3	2	3	0	2
m	0	-2	-1	0	-1	-3	2	3	0	-2

Exercise 2

Consider the elements: ${}_{29}\text{Cu}$, ${}_{35}\text{Br}$, ${}_{42}\text{Mo}$, ${}_{54}\text{Xe}$.

1. Provide the electronic structures of these elements.
2. Locate these elements in the periodic table.
3. Which of these elements are transition metals?
4. Which element is chemically inert, indicate its external structure.
5. Assign and explain the values of the first ionization energies (IE) and electronegativities (χ) of the following elements: Cu, Br, and Mo.

IE (eV)	7,7	11,8	7,2
χ	1,9	2,8	1,8

6. An element belongs to the sixth period and group IV_B. What is its electronic structure? Give its atomic number

Exercise 3

Consider the elements of the periodic table:

Element A	Transition metal belonging to group 1 and the same period as ${}_{26}\text{Fe}$ (Iron).
Element B	Alkali metal from the 5 th period.
Element C	Belongs to the same period as ${}_{13}\text{Al}$ and the same group as ${}_{7}\text{N}$.
Element D	Non metal whose last (highest energy) subshell is $3p^4$.
Element E	Has a single electron characterized by the quantum numbers (3, 2, -2, 1/2).

1. For each element, provide: the electron configuration, the period, the group, and the subgroup.
2. Provide the quantum numbers of the single (unpaired) electron of B.

3. Assign to each element its atomic radius and electronegativity from the following values:

R (Å)	1.00	1.25	1.35	1.60	2.35
χ	0.82	1.36	1.90	2.19	2.58

Exercise 4

1. Calculate the energy of the lithium atom (${}^3\text{Li}$) and those of the Li^+ , Li^{2+} and Li^{3+} ions in their ground states.
2. Deduce the different ionization energies.

		Electron "j"	
		1s	2s2p
Electron "i"	1s	0,31	0
	2s2p	0,85	0,35

Correction

Exercise 1

a: $n = 2, l = 0, m = 0 \rightarrow$ Valid. Subshell: 2s.

b: $n = 4, l = 1, m = -2 \rightarrow$ m must be between -1 and 1 . $m = -2 \rightarrow$ Invalid.

c: $n = 3, l = 1, m = -1 \rightarrow$ Valid. Subshell: 3p.

d: $l = -1 \rightarrow$ Invalid because l cannot be negative.

e: $l = 0 \rightarrow$ m must be 0. $m = -1 \rightarrow$ Invalid.

f: $n = 5, l = 3, m = -3 \rightarrow$ Valid. Subshell: 5f.

g: $n = 4, l = 2, m = 2 \rightarrow$ Valid. Subshell: 4d.

h: $n = 2, l = 3 \rightarrow$ Invalid because $l \geq n$.

i: $n = 3, l = 0, m = 0 \rightarrow$ Valid. Subshell: 3s.

j: $n = 5, l = 2, m = -2 \rightarrow$ Valid. Subshell: 5d.

Exercise 2

1. Electronic structures and location of these elements in the periodic table.

Element	Electronic structure	Period	Group
$_{29}\text{Cu}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	4	I _B
$_{35}\text{Br}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	4	VII _A
$_{42}\text{Mo}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^5$	5	VI _B
$_{54}\text{Xe}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$	5	VIII _A

3. The transition metals are: $_{29}\text{Cu}$, and $_{42}\text{Mo}$ because they have an incomplete (d) subshell.

4. The chemically inert element is an element with all its sub-shells fully occupied by electrons. So: xenon ($_{54}\text{Xe}$) is the inert element (rare gas). Its external structure is: $5s^2 4d^{10} 5p^6$

5. $\text{IE}(\text{Br}) > \text{IE}(\text{Cu}) > \text{IE}(\text{Mo})$; and; $\chi(\text{Br}) > \chi(\text{Cu}) > \chi(\text{Mo})$.

Element	IE	X
Br	11,8	2,8
Cu	7,7	1,9
Mo	7,2	1,8

6. The element belongs to the 6th period, so: $n = 6$

And in group IV_B, therefore: it has 4 electrons in the outer sub-shell.

Chapter 3

The structure of its outer shell (valence shell) is: $6s^2 4f^{14} 5d^2$

Hence, the electronic configuration is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$

Its atomic number is: $Z = 72$; and the element is: ${}_{72}\text{Hf}$.

Exercise 3

1. Electronic structures and location of these elements in the periodic table.

Element	Electronic structure	Period	Group
A	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	4	I _B
B	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$	5	I _A
C	$1s^2 2s^2 2p^6 3s^2 3p^3$	3	V _A
D	$1s^2 2s^2 2p^6 3s^2 3p^4$	3	VI _A
E	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	4	III _B

${}_{26}\text{Fe}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 \longrightarrow$ Period = 4

${}_{13}\text{Al}$: $1s^2 2s^2 2p^6 3s^2 3p^1 \longrightarrow$ Period = 3

${}_{7}\text{N}$: $1s^2 2s^2 2p^3 \longrightarrow$ Group = V_A

2. The quantum numbers of the single (unpaired) electron of B.

$\uparrow$ $5s^1$: $n = 5, l = 0, m = 0, s = +1/2$

3. Assign atomic radius and electronegativity

Group \ Period	I _A	III _B	I _B	V _A	VI _A
n = 3				C	D
n = 4		E	A		
n = 5	B				

Atomic radius: $D < C < A < E < B$

Electronegativity: $B < E < A < C < D$

Element	A	B	C	D	E
R (Å)	1,35	2,35	1,25	1,00	1,60
χ	1,90	0,82	2,19	2,58	1,36

Exercise 4**1. Calculation of the energy of the lithium atom (${}_3\text{Li}$)**

$${}_3\text{Li}: 1s^2 2s^1$$

$$E_{\text{Li}} = 2 \times E_{1s} + 1 \times E_{2s}$$

$$Z_{\text{eff}} = Z - \Sigma \sigma_{ij}, E_n = \frac{-13,6 \times Z_{\text{eff}}^2}{n^2}$$

$$Z_{\text{eff}}(1s) = Z - \sigma_{1s-1s} = 3 - 0,31 = 2,69$$

$$E_{1s} = \frac{-13,6 \times (2,69)^2}{1^2} = -98,4109 \text{ eV}$$

$$Z_{\text{eff}}(2s) = Z - \sigma_{2s-1s} = 3 - 2 \times 0,85 = 1,3$$

$$E_{2s} = \frac{-13,6 \times (1,3)^2}{2^2} = -5,746 \text{ eV}$$

$$E_{\text{Li}} = 2 \times E_{1s} + 1 \times E_{2s} = 2 \times (-98,4109) + 1 \times (-5,746) = -202,5678 \text{ eV}$$

- Calculation of the energy of Li^+

$${}_3\text{Li}^+: 1s^2, Z_{\text{eff}}(1s) = 2,69$$

$$E_{\text{Li}^+} = 2 \times E_{1s} = 2 \times (-98,41096) = -196,82192 \text{ eV}$$

- Calculation of the energy of Li^{2+}

$${}_3\text{Li}^{2+}: 1s^1$$

Li^{2+} is a Hydrogen-like ion

$$E_{\text{Li}^{2+}} = \frac{-13,6 \times Z^2}{n^2} = \frac{-13,6 \times 3^2}{1^2} = -122,4 \text{ eV}$$

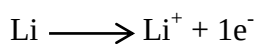
- Calculation of the energy of Li^{3+}

$${}_3\text{Li}^{3+}: 1s^0$$

$$E_{\text{Li}^{3+}} = 0 \text{ eV}$$

2. Calculation of the different ionization energies

1st ionization



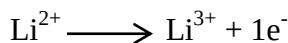
$$\text{IE}_1 = E_{\text{Li}^+} - E_{\text{Li}} = +5,74588 \text{ eV}$$

2nd ionization

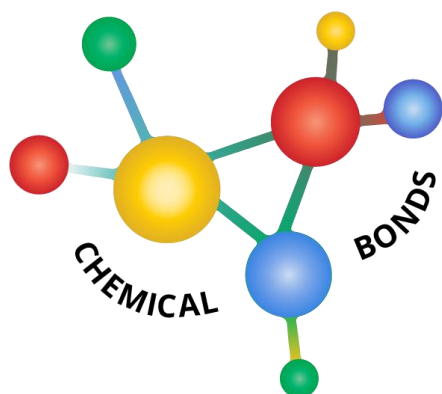


$$\text{IE}_2 = E_{\text{Li}^{2+}} - E_{\text{Li}^+} = +74,42192 \text{ eV}$$

3rd ionization

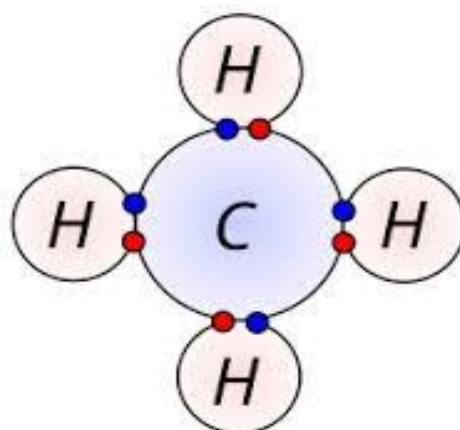


$$\text{IE}_3 = E_{\text{Li}^{3+}} - E_{\text{Li}^{2+}} = +122,4 \text{ eV}$$



Chapter 4

Chemical bonds



Chapter 4

Chemical bonds

Introduction

In nature, the only elements found in the form of free, isolated atoms are the inert gases or noble gases (Group VIII_A), which are very stable. This stability is due to their completely filled outer shell, which contains 8 electrons. The only exception is helium, which has a single shell filled with 2 electrons. All the other remaining atoms in the periodic table bond together to form molecules, ionic compounds, or metals, which are more stable than isolated atoms.

An atom whose outer shell is not complete is not stable. To reach this state of stability, it will bind with other atoms:

- either by giving its outer electrons to other atoms,
- or by taking the electrons from these other atoms,
- or by sharing the electrons of these other atoms.

All of this falls under the objectives of studying **chemical bonds**.

The term "**bond**" refers to all interactions that lead atoms to form a molecule that is more stable than themselves in their ground state. The resulting molecule will then be in the lowest possible energy state. This bond is formed through valence electrons. Its nature depends essentially on the electronegativity of the atoms.

4.1. Covalent bonding in Lewis theory

A covalent bond is the sharing of one or more pairs of electrons (an electron pair) between two atoms (**Fig. 4.1**). These atoms have similar electronegativity (χ). The shared electron pair, or bonding pair, is the basis of the covalent bond formed between the two atoms. A covalent bond is represented by a dash between the two atoms involved.

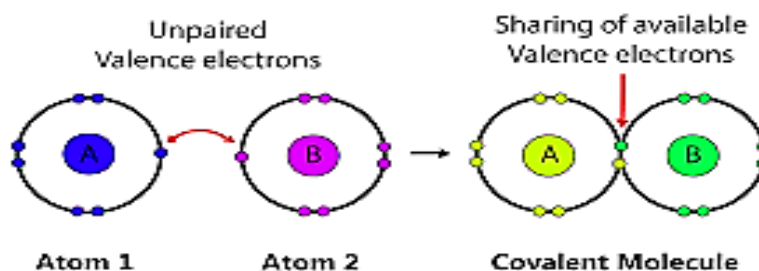
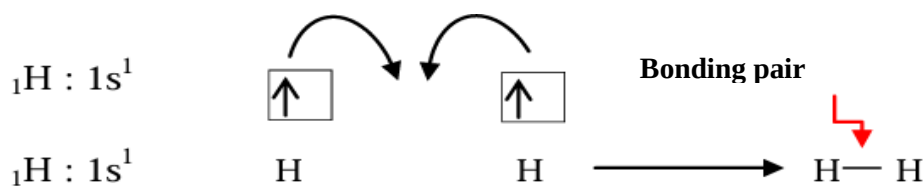


Figure 4.1: Formation of covalent bond.

Example: H_2



4.1.1. Valence electrons - Valence shell

The valence of a chemical element is the number of chemical bonds it can form. This concept is directly related to the electron configuration of the valence electrons of the element in question, these are the electrons in the outermost shell, called the valence shell or peripheral shell (**Fig. 4.2**). It is equal to the number of unpaired (lone) electrons.

The presence of lone pairs of electrons, unpaired electrons, or empty atomic orbitals (vacant slots) in this shell determines the chemical properties of a given element.

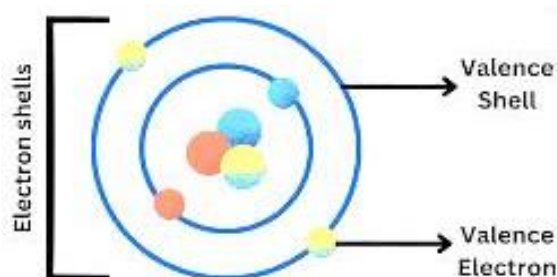


Figure 4.2: Valence electrons and valence shell.

Example:

Hydrogen: $1s^1 \rightarrow \text{valence} = 1$

Oxygen: $\text{O} (Z=8) \rightarrow 1s^2 2s^2 2p^4 \rightarrow \text{valence} = 2$



4.1.2. Octet Rule

The Octet Rule states that atoms tend to gain, lose, or share electrons to achieve a full valence shell of eight electrons. This stable configuration is equivalent to that of the nearest noble gases (ns^2np^6). A key exception is hydrogen, which seeks to achieve the duet configuration of helium, with only two electrons.

This rule has many exceptions, such as:

- **Incomplete Octet:** This applies to a few elements from the second period (e.g., B, Be). For instance, the boron atom is surrounded by 6 electrons (e.g., BF_3).
- **Expanded Octet:** This applies to some elements from the third period (e.g., P, S). For example, in PCl_5 , the phosphorus atom is surrounded by 10 electrons.

4.1.3. Lewis diagram

Lewis diagram (also commonly known as a Lewis structure or Lewis dot diagram) is a graphical representation used in chemistry to show the valence electrons of atoms and how they are arranged in a molecule or polyatomic ion. It illustrates the bonding between atoms and any lone pairs of electrons that may exist.

In the Lewis representation of covalent bonding, only the outer electrons (valence electrons) participate in bond formation and are represented by dots. The valence electrons of atoms are paired into bonds (or lone pairs), which are depicted using lines.

4.1.3.1. General method for constructing Lewis structures

- Write the electron configuration (by shell) for each atom.
- Determine the number of valence electrons for each atom and represent them using orbital box diagrams.
- Choose the central atom: Select the atom with the highest number of unpaired electrons. If two atoms have the same number of unpaired electrons, the central atom is the one with the lower electronegativity (except hydrogen).
- Distribute the electron pairs in the molecule into bonding pairs BP (forming covalent bonds) and lone pairs (nonbonding pairs) NBP, respecting the Octet Rule.
- For molecular ions, assign the negative charge (–) to the most electronegative atom and the positive charge (+) to the least electronegative atom.

4.1.3.2. Lewis diagram of atoms

To facilitate the representation of chemical bonds, we use symbols that show only the valence electrons (Lewis symbols). These are identical for all elements in the same group of the periodic table (**Fig. 4.3**).

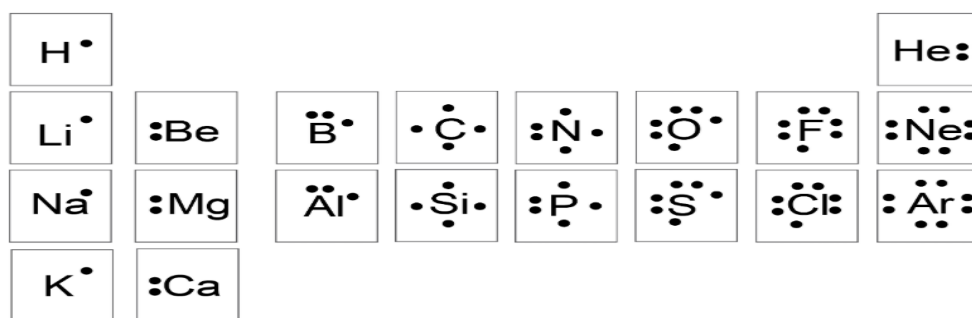
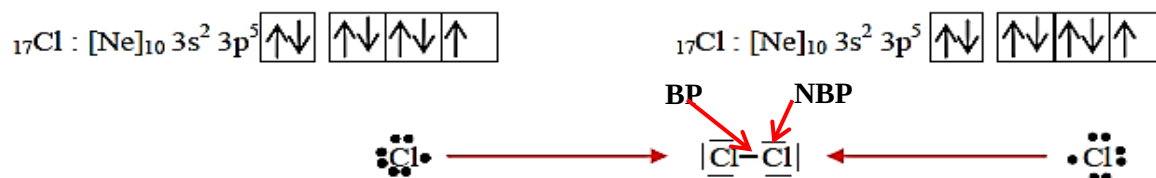


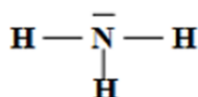
Figure 4.3: Lewis diagram of atoms.

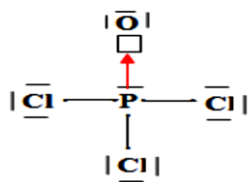
4.1.3.3. Lewis diagram of molecules

Examples

1. Cl₂

Total number of electron pairs around Cl = 4 pairs (1 bonding pair (BP) and 3 lone pairs or Non-bonding pair (NBP)), meaning 8 electrons. The octet rule is satisfied.

2. O₂: Formation of a single σ covalent bond and a π bond.3. N₂: Formation of a single σ covalent bond and two π bonds.4. H₂O5. NH₃

6. PCl_3O 

4.1.4. Different types of chemical bonds

To classify chemical bonds, the two essential concepts are bond energies (or their opposites: dissociation energies) and the electronegativities of the bonded atoms. There are strong bonds and weak bonds (**Fig. 4.4**):

Strong bonds: three types are distinguished

- The covalent bond
- The ionic bond
- The metallic bond

Weak bonds: there are two types

- The hydrogen bond
- Van Der Waals interaction

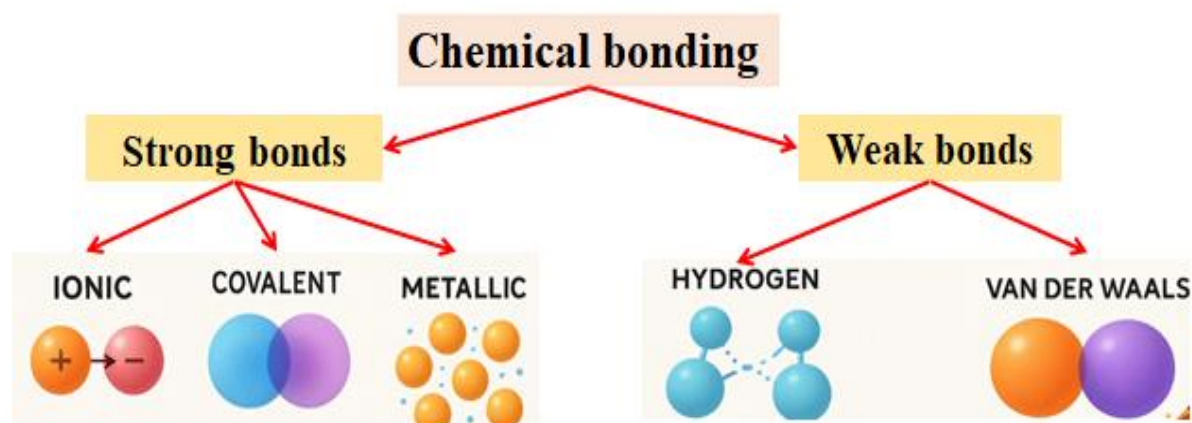


Figure 4.4: Different types of chemical bonds.

4.1.4.1. Strong bonds

a. Covalent bond

A covalent bond, formed by the sharing of two electrons between two atoms, is represented by a dash between them.

a.1. Non polar covalent bond

A nonpolar covalent bond involves an equal sharing of electrons between two identical atoms or between two atoms if the electronegativity difference between them is less than 0,4, with each atom providing one valence electron.

Covalent bonds are classified by their bond order. A single bond consists of one shared electron pair, a double bond consists of two, and a triple bond consists of three. The stability and strength of the bond increase with the number of shared pairs.

Examples

Single covalent bond: Cl_2

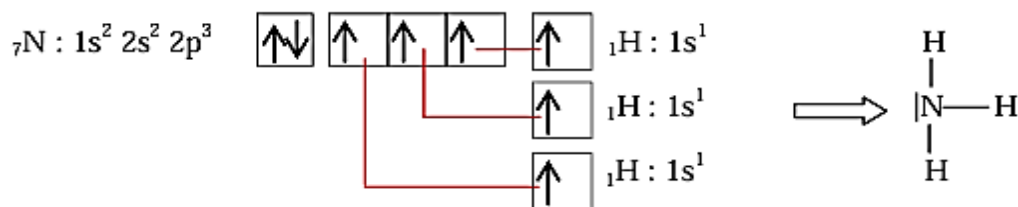
Double covalent bond: O_2

Triple covalent double: N_2

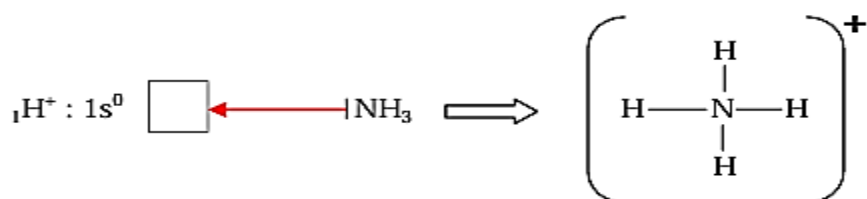
a.2. Coordinate or dative covalent bond

One of the two atoms (the donor: A) provides a pair of electrons from its outer shell. The other (the acceptor: B) receives this pair in an empty orbital of its outer shell. The dative bond is identical to a covalent bond; however, it is represented by an arrow pointing from the donor to the acceptor. $\text{A} \uparrow\downarrow \text{B} \longrightarrow \text{A} - \text{B}$

Example: The ammonium ion NH_4^+ is the combination of NH_3 and H^+ .



It is the non-bonding pair that will participate in the dative bond:



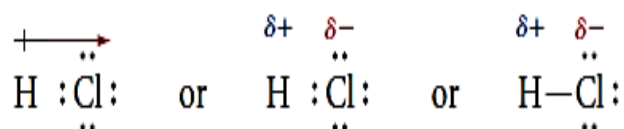
a.3. Polar covalent bond

Covalent bonds can be formed not only between identical atoms ($\text{H} - \text{H}$, $\text{C} - \text{C}$) but also between different atoms ($\text{C} - \text{H}$, $\text{C} - \text{Cl}$), provided that the atoms do not differ too greatly in

electronegativity. However, if the atoms are different from one another, the electron pair may not be shared equally between them. Such a bond is sometimes called a **polar covalent bond** because the atoms that are linked carry a partial negative and a partial positive charge.

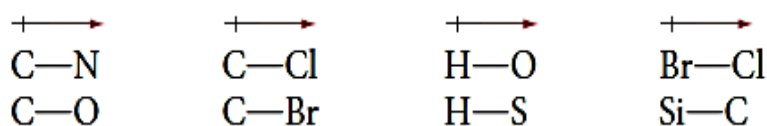
Example

The hydrogen chloride molecule provides an example of a polar covalent bond. Chlorine atoms are more electronegative than hydrogen atoms, but even so, the bond that they form is covalent rather than ionic. However, the shared electron pair is attracted more toward the chlorine, which therefore is slightly negative with respect to the hydrogen. This bond polarization is indicated by an arrow whose head is negative and whose tail is marked with a plus sign. Alternatively, a partial charge, written as $\delta+$ or $\delta-$ (read as “delta plus” or “delta minus”), may be shown:



The bonding electron pair, which is shared *unequally*, is displaced toward the chlorine.

Example



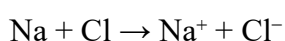
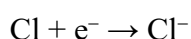
b. Ionic bond

Ionic bonding is important between atoms of vastly different electronegativity ($\Delta\chi \geq 1,7$). The bond results from one atom giving up an electron while another atom accepts the electron. There is no sharing of electrons between the two atoms that form the bond, but rather a transfer of electrons from one atom to another.

Note: Ionic bonds are formed between elements with very low electronegativity that are electron donors (**IA**, **IIA**), and elements with very high electronegativity that are electron acceptors (**VI_A**, **VII_A**).

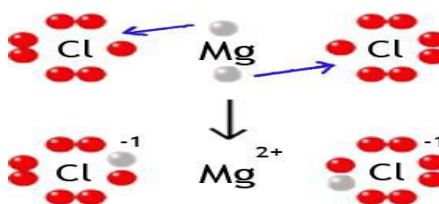
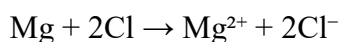
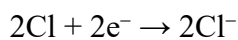
Example 1

The overall reaction is a transfer of one electron:



Example 2

The overall reaction is:

**c. Metallic bond**

A metallic bond is the electrostatic attraction between a lattice of positive metal ions and a sea of delocalized electrons, which are valence electrons not bound to any specific atom (**Fig. 4.5**). This unique bonding model grants metals their characteristic properties: high electrical and thermal conductivity (due to mobile electrons), malleability and ductility (as electron sea allows ion layers to slide), luster (from light interaction with free electrons), and generally high melting points (requiring significant energy to break the bonds). Common examples include the strong structure of iron, excellent conductivity of copper, and lightweight malleability of aluminum.

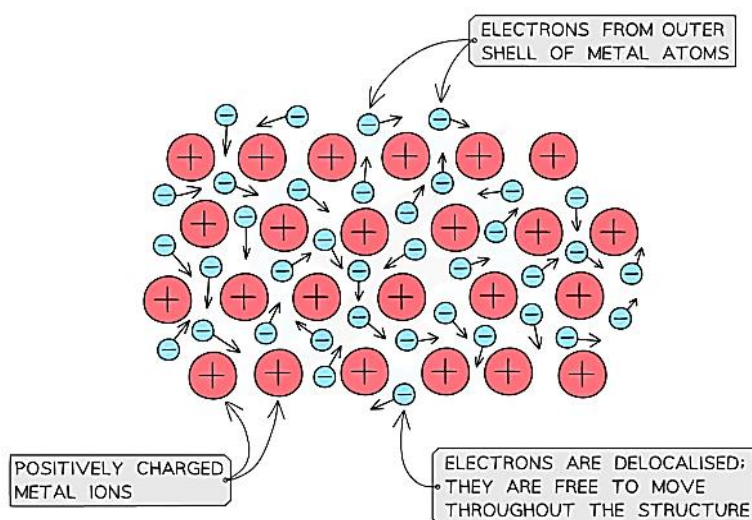


Figure 4.5: Metallic bonding.

4.1.4.2. Weak bonds**a. Hydrogen Bonding**

A hydrogen bond is a particularly strong type of dipole-dipole attraction. It occurs when a hydrogen atom is covalently bonded to a highly electronegative atom specifically nitrogen (N), oxygen (O), or fluorine (F). This bond polarizes the molecule, giving the hydrogen atom a significant partial positive charge (δ^+). This hydrogen is then strongly attracted to a lone

pair of electrons in another electronegative atom (N, O, or F) in a different molecule or a different part of the same large molecule (**Fig. 4.6**). Its importance is immense; hydrogen bonding is responsible for the unique properties of water, such as its high boiling point and surface tension. It is also the fundamental force that holds the two strands of the DNA double helix together and determines the three-dimensional shape of proteins.

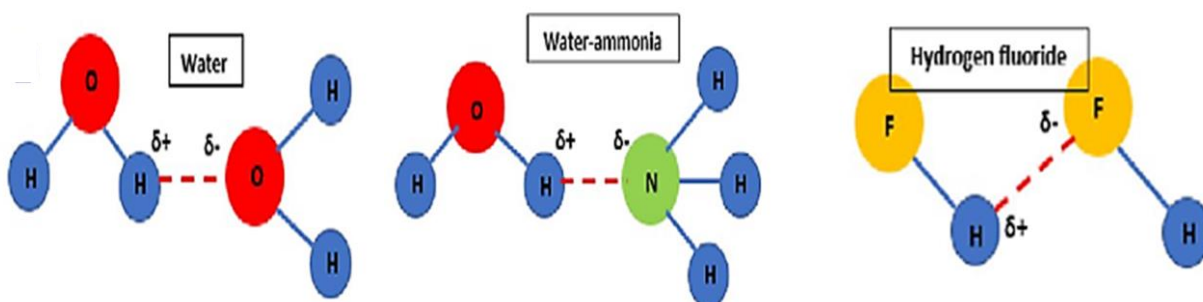


Figure 4.6: Hydrogen Bonding.

b. Van der Waals bonds

Van der Waals (VdW) forces are weak, short-range electrostatic attractive forces between uncharged molecules, arising from interactions between temporary or permanent molecular dipoles. They are among the weakest of the intermolecular forces, but they are fundamental to many physical and biological processes. Think of them as the universal "glue" that acts between all atoms and molecules, even noble gas atoms and nonpolar molecules like methane (CH_4) or carbon dioxide (CO_2).

Van der Waals forces are actually a composite of three distinct types of interactions:

b.1. Keesom Forces (Dipole-Dipole)

Dipole-dipole forces are the attractive interactions between the permanent dipoles of neighboring polar molecules, where the positive end of one molecule is attracted to the negative end of another (**Fig. 4.7**).

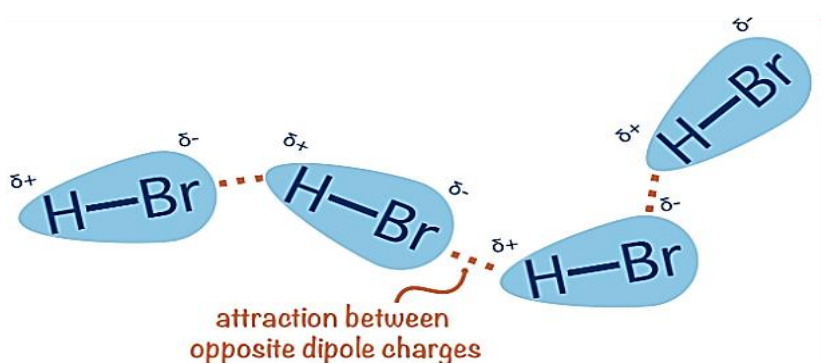


Figure 4.7: Keesom Forces.

b.2. Debye Forces (Dipole-Induced Dipole)

The attraction between a permanent dipole in one molecule and an induced dipole in a neighboring molecule (Fig. 4.8).

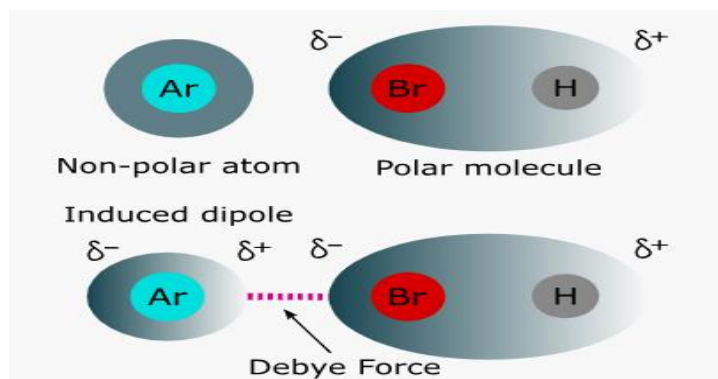


Figure 4.8: Debye Forces.

b.3. London Dispersion Forces (Induced Dipole-Induced Dipole)

London dispersion forces are the weakest type of intermolecular attraction. The attraction arising from temporary, instantaneous dipoles in nonpolar molecules or atoms (Fig. 4.9).

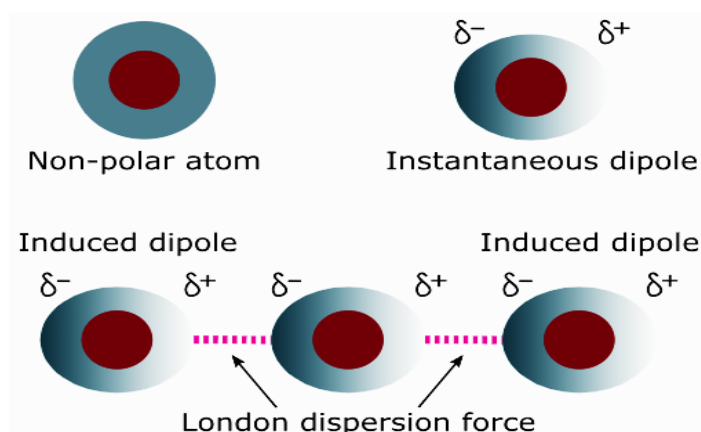


Figure 4.9: London Dispersion Forces.

4.2. Polarization, dipole moments, and partial ionic character of the bond

4.2.1. Polarity and polarization of bonds

- When a covalent bond unites two identical atoms (X-X), the electron pair is shared between the two atoms. The electron cloud is distributed equally over the two atoms.

There is therefore no polarity ($\mu = 0$).



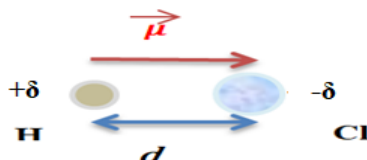
- If the two atoms are different (X-Y), it is the more electronegative atom that attracts the electron pair. The electron cloud is no longer symmetrical: it is moved towards the more electronegative atom: we say that the more electronegative atom polarizes the electron cloud. Partial charges are created on the atoms: δ^+ on the less electronegative atom and δ^- on the more electronegative atom. $\delta^+ \text{X} : \text{Y} \delta^-$.



The X-Y bond is polarized. It exhibits permanent polarization, characterized by its dipole moment μ .

4.2.2. Dipole moment

The polarization of a bond is characterized by the value of the charges δ^+ and δ^- , but also by the direction and value of its electric moment, or dipole moment μ . It is characterized by a vector and oriented, by convention, from the positive charge to the negative charge.



The dipole moment (μ) is defined by the relation: $\mu = q \times d$

With : $+q = +\delta \times e$

$-q = -\delta \times e$

$$\mu = |\delta| \times e \times d$$

Where:

δ : the partial charge ($0 < \delta < 1$).

d : the distance separating the two charges (bond length, m).

In the SI unit system, μ is expressed in Coulomb-meter (C.m), or in Debye (D):

$$1\text{D} = 3,33 \times 10^{-30} \text{ C.m}$$

- **Nonpolar molecules (A_2 molecules)**

$$\mu = 0$$

Example : H_2

- **Polar molecules (AB molecules)**

$$\mu \neq 0$$

Example : HCl

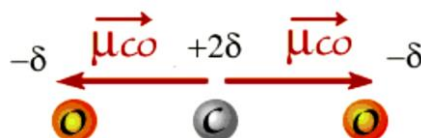
- **AB₂ molecules**

➤ **Linear AB₂ molecules**

Any molecule with a center of symmetry has a zero dipole moment.

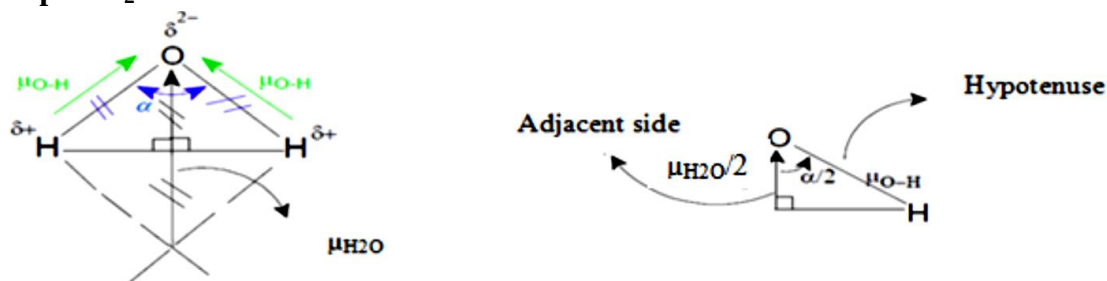
$$\mu = 0$$

Example : CO₂



➤ **Angular AB₂ molecules**

Example: H₂O

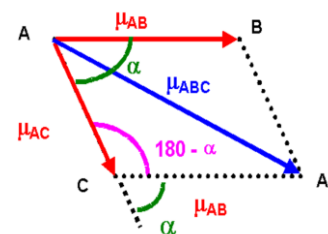


$$\cos (\alpha / 2)=\left(\mu_{\text {H}_2 \text {O}} / 2\right) / \mu_{\text {O-H }} \Leftrightarrow \mu_{\text {H}_2 \text {O}}=2 \times \mu_{\text {O-H }} \times \cos (\alpha / 2)$$

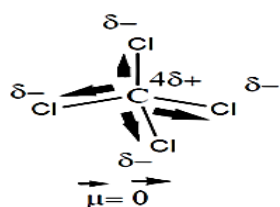
- **ABC molecule**

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

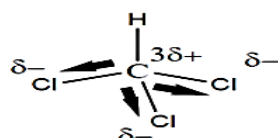
$$\mu_{\text {ABC }}=\mu_{\text {AB }}^2+\mu_{\text {AC }}^2-2 \mu_{\text {AB }} \times \mu_{\text {AC }} \times \cos \left(180-\alpha\right)$$



Example

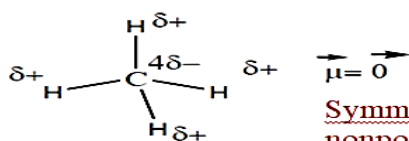


Symmetric
nonpolar molecule



$$\vec{\mu}=\vec{\mu}_1+\vec{\mu}_2+\vec{\mu}_3+\vec{0}=1,11 \text { D}$$

Asymmetric polar
molecule

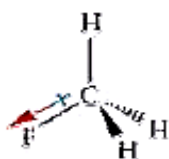


Symmetric
nonpolar molecule

Exercise

Determine whether the molecules CH_3F and CF_4 are polar or nonpolar.

- For the CH_3F molecule, its geometry is that of a tetrahedron. The three C-H bonds are considered to be non-polar covalent bonds, having no significant dipole. On the other hand, the C-F bond is a polar covalent bond in which the dipole points towards the most electronegative element, fluorine. Overall, the molecule is polar, since there is a non-zero dipole (vector).



There is only one vector. So the sum of the vectors is not equal to 0. The molecule is polar.

- For the CF_4 molecule, its geometry is also tetrahedral. However, here, the four C-F bonds are polar covalent. The dipole points to the fluorine atom, the most electronegative, for the four bonds. By summing these vectors (add the vectors two by two), they cancel each other out. The resulting dipole is then zero, and the molecule is globally non-polar.

4.2.3. Partial ionic character of the bond

The determination of the ionic character of a bond requires knowledge of its dipole moment.

It is given by the following relation:

$$\text{P.I.C} = \frac{\mu_{\text{Experimental}}}{\mu_{\text{theoretical}}} \times 100 = \frac{\delta \times e \times d}{e \times d} \times 100 = \delta \times 100$$

If:

P.I.C = 50% ($\delta = 0,5$): the bond is 50% ionic,

P.I.C = 100% ($\delta = 1$): the bond is purely ionic,

P.I.C = 0% ($\delta = 0$): the bond is purely covalent.

Exercise

In the water molecule, the experimental H-O-H angle is 105° .

1. Calculate the dipole moment of this molecule, considering it is equal to the vector sum of the dipole moments of the two O-H bonds.
2. Calculate the ionic percentage of the O-H bond in H_2O . Given: $\mu(\text{O-H}) = 1,51 \text{ D}$ and $d(\text{O-H}) = 0,96 \text{ \AA}$.

Correction

1. Calculation of the dipole moment of the H₂O molecule

$$\mu_{H_2O} = 2 \times \mu_{OH} \times \cos(\alpha/2) = 21,51 \times \cos(105/2) = 1,84 \text{ Debye}$$

2. Ionic percentage of the O-H bond in H₂O.

$$\text{The ionic percentage} = (\mu_{\text{experimental}} / \mu_{\text{theoretical}}) \times 100\%$$

The theoretical dipole moment is calculated as: $\mu_{\text{theoretical}} = e \times d$.

$$\mu_{\text{theoretical}} = 1,602 \times 10^{-19} \times 0,96 \times 10^{-10} = 1,538 \times 10^{-29} \text{ C}\cdot\text{m}$$

The Debye (D) is a more convenient unit for dipole moments. $1 \text{ D} = 3,336 \times 10^{-30} \text{ C}\cdot\text{m}$.

Therefore, we convert $\mu_{\text{theoretical}}$ to Debyes:

$$\mu_{\text{theoretical}} = 1,538 \times 10^{-29} / 3,336 \times 10^{-30} \approx 4.61 \text{ D}$$

$$\mu_{\text{O-H}} = 1,51 \text{ D and } d_{\text{O-H}} = 0,96 \text{ \AA.}$$

$$\% \text{ ionique} = (1,51/4,61) \times 100 = 32,8 \%$$

The bond is 33% ionic

4.3. Molecular geometry: Gillespie theory or VSEPR

The Lewis structure representation of molecules allows for the determination of atom arrangement and covalent bonds between them, but it does not predict the actual geometry of the molecules. For this, it is necessary to use a theory that takes into account the repulsion between electron pairs around the central atom to predict the three-dimensional shape of the molecule.

The VSEPR theory (Valence Shell Electron Pair Repulsion) is one of the most widely used theories in chemistry for predicting molecular geometry. It is based on the idea that electron pairs around a central atom repel each other in order to minimize electron-electron interactions and achieve the most stable electron configuration possible.

Using the VSEPR Method

Rule 1: We focus on all the electron pairs in the valence shell of the central atom "A". We denote "m" as the number of bonding pairs (which participate in bonding) and "n" as the number of non-bonding (lone) pairs (which do not participate in bonding). The total number of pairs is noted as (m+n). We then write the notation as AX_mE_n (**Fig. 4.10**).

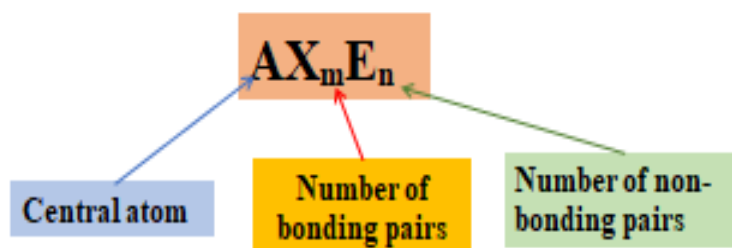


Figure 4.10: VSEPR representation of molecules.

How do we choose the central atom?

1st condition: Choose the atom with the smallest stoichiometric coefficient. If the above is not applicable, move to the second condition.

2nd condition: Choose the atom with the highest number of unpaired electrons. If the above is not applicable, move to the third condition.

3rd condition: Choose the atom with the highest atomic number Z .

- Example of the CH_4 molecule**

The central atom is C $\Rightarrow \text{A}$ (C_1H_4 ; the 1st condition was sufficient to choose atom C)

The bonded atom is H, with $m = 4$ bonding pairs $\Rightarrow \text{X}_4$

The C atom in this molecule has no lone pairs ($n = 0$) $\Rightarrow \text{E}_n = 0$

$\Rightarrow \text{CH}_4$, will have the geometric form AX_4 .

- Example of the NH_3 molecule**

The central atom is N $\Rightarrow \text{A}$ (Choice of the central atom according to the 1st condition)

The bonded atom is H, with $m = 3$ bonding pairs $\Rightarrow \text{X}_3$

The N atom in this molecule has 1 lone pair ($n = 1$) $\Rightarrow \text{E}_n = \text{E}$

$\Rightarrow \text{NH}_3$, will have the geometric form AX_3E

Rule 2: If the molecule has multiple bonds (double π bond or triple σ, π bond), each bond will be considered as a single (σ) bond:

- $\text{C}=\text{C} \Rightarrow 2$ single bonds $\Rightarrow 1$ bonding pair

- $\text{C}\equiv\text{C} \Rightarrow 3$ single bonds $\Rightarrow 1$ bonding pair

- Example of the C_2H_4 molecule**

$\text{H}_2\text{C}=\text{CH}_2$:

The central atom is C $\Rightarrow \text{A}$

The C atom is bonded to 2 H and 1 C, with $m = 3$ bonding pairs $\Rightarrow X_3$

$n = 0$ (no lone pairs) $\Rightarrow E_n = 0$

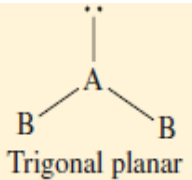
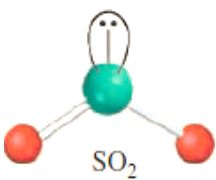
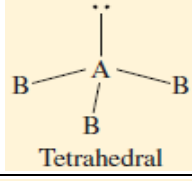
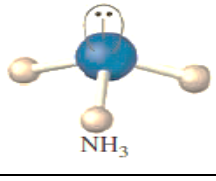
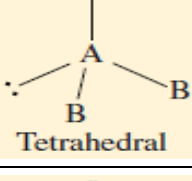
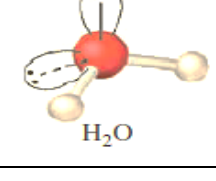
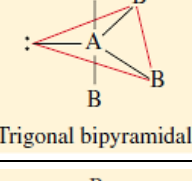
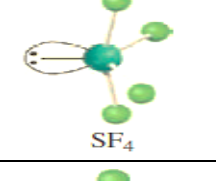
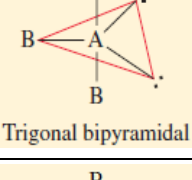
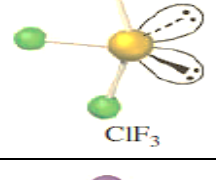
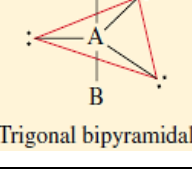
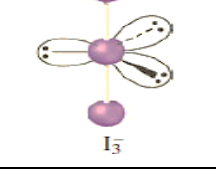
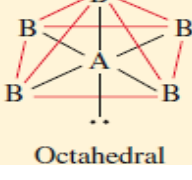
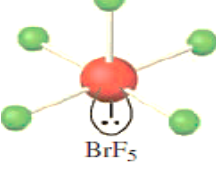
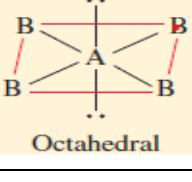
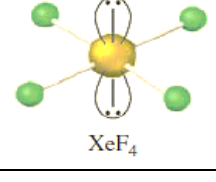
$\Rightarrow C_2H_4$, will have the geometric form AX_3 for each carbon atom.

Rule 3: In the molecule, electron pairs are not equivalent

- A lone pair (or non-bonding pair) is more repulsive than a bonding pair.
- A multiple bond (double, triple) is more repulsive than a single bonding pair.
- An electronegative atom is more repulsive than an electropositive atom.
- In molecules such as CH_4 , NH_3 , and H_2O , for example, the basic shape of these molecules is tetrahedral, but the bond angles between the atoms are different. Decreasing from $109^\circ 28'$ for methane, to $107^\circ 6'$ for ammonia, and further down to $104^\circ 5'$ for water: this is due to the repulsive effect of the lone pair in ammonia and the two lone pairs in water.
- As the number of lone pairs increases, the repulsion between them increases, which leads to a decrease in the bond angles of the molecular geometry and results in a distortion of the structure.
- In general, to determine the hybridization of a molecule from its geometry AX_mE_n , the procedure is as follows:
 - If $m+n = 2 \Rightarrow$ Hybridization of one s AO and one p AO $\Rightarrow sp$ hybridization.
 - If $m+n = 3 \Rightarrow$ Hybridization of one s AO and two p AO $\Rightarrow sp^2$ hybridization.
 - If $m+n = 4 \Rightarrow$ Hybridization of one s AO and three p AO $\Rightarrow sp^3$ hybridization.
 - If $m+n = 5 \Rightarrow$ Hybridization of one s AO, three p AO, and one d AO $\Rightarrow sp^3d$ hybridization.
 - If $m+n = 6 \Rightarrow$ Hybridization of one s AO, three p AOs, and two d AO $\Rightarrow sp^3d^2$ hybridization.

The following table (**Table 4.1**) provides some examples of molecular geometries.

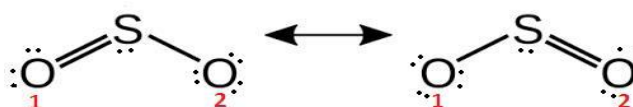
Table 4.1: Geometry of simple molecules and ions.

Class of molecule	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs*	Geometry	Examples
AX_2E	3	2	1	 Trigonal planar	Bent	 SO_2
AX_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH_3
AX_2E_2	4	2	2	 Tetrahedral	Bent	 H_2O
AX_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AX_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3
AX_2E_3	5	2	3	 Trigonal bipyramidal	Linear	 I_3
AX_5E	6	5	1	 Octahedral	Square pyramidal	 BrF_5
AX_4E_2	6	4	2	 Octahedral	Square planar	 XeF_4

Limitations of the Lewis Model

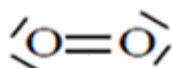
The Lewis model facilitates the understanding of the covalent bond and, when combined with the Gillespie theory, it constitutes a valuable tool for structural chemistry. However, it has certain limitations:

- As can be observed in the previous examples, bonding does not always lead to the noble gas octet.
- It sometimes introduces an asymmetry in the molecule that does not exist in reality. For example, the sulfur-oxygen bonds are identical in SO_2 , whereas the Lewis diagram predicts one double bond and one single bond. This leads to the use of the notation:



and to the consideration that the actual structure resonates between the 2 limiting formulas, or mesomeric forms. The S-O bond is intermediate between a single bond and a double bond.

- Lewis diagrams do not predict the existence of unpaired electrons. However, certain molecules, such as NO or H_2^+ , have an odd number of electrons. Other molecules, like O_2 , although they have an even number of electrons, do not have the predictable simple Lewis diagram:



because their magnetic properties indicate the presence of unpaired electrons.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are not viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a **quantum mechanical model**.

4.4. Chemical bonds in the quantum model

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called orbitals, each with a particular orbital energy. Just as the positions and energies of electrons in atoms can be described in terms of atomic orbitals (AOs), the positions and energies of electrons in molecules can be described in terms of molecular orbitals (MOs). A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called **molecular orbital theory** is a delocalized approach to bonding.

4.4.1. Molecular Orbital Theory (LCAO method)

This theory is based on the **Linear Combination of Atomic Orbitals (LCAO)**. Its main advantage is that it provides a more generalized representation of the molecule. From two atomic orbitals originating from two atoms, two molecular orbitals are constructed, which will form the molecule.

4.4.1.1. Bonding Molecular Orbital

e^- from atom A $\Psi_{1s} = 1s_A$; e^- from atom B $\Psi_{1s} = 1s_B$ (**Fig. 4.11**).

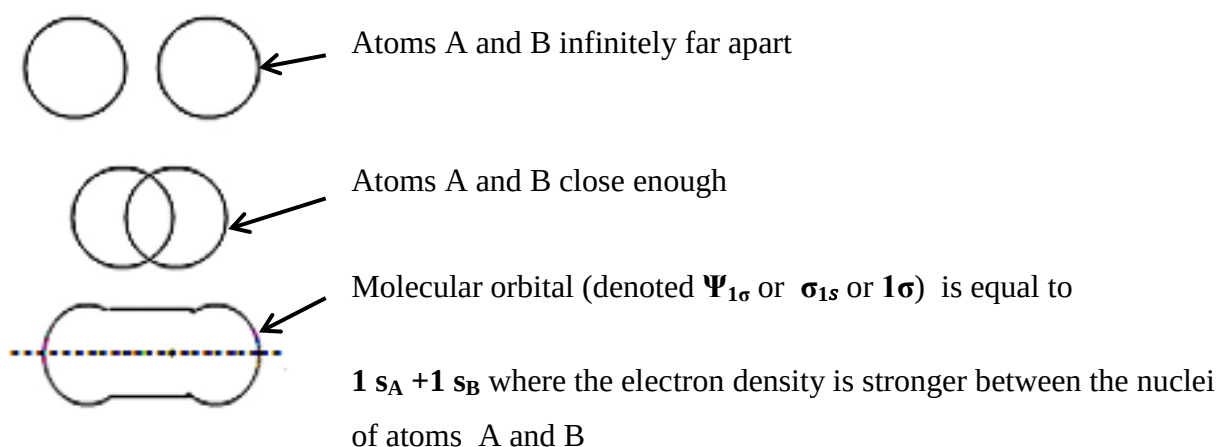


Figure 4.11: Bonding Molecular Orbital.

Bonding σ orbital;

$$\Psi_{1\sigma} = \Psi_{1sA} + \Psi_{1sB} \text{ or } \sigma_{1s} = 1s_A + 1s_B$$

The first possible combination of two atomic orbitals is addition. If we square $(1s_A + 1s_B)$ we get:

$$(1s_A + 1s_B)^2 = 1s_A^2 + 1s_B^2 + 2 \times 1s_A 1s_B$$

This expression represents the probability of electron presence in the molecular orbital. The sum $1s_A^2 + 1s_B^2$ represents the probabilities of presence in the two separate atoms. It is observed that the surface representing the electron density in the molecular orbital is larger than the sum of the electron densities in the orbitals of the separated atoms (**Fig. 4.12**). Therefore, the electrons will be located between the two nuclei in a region of strong attraction, and the energy of the system (2 protons, 2 electrons) is lowered. These results in a decrease in the energy of the molecular orbitals compared to the energy of the orbitals of the isolated atoms. This orbital is said to be bonding since the conditions for bonding between the two atoms are fulfilled; the electrons occupy the space between the two nuclei.

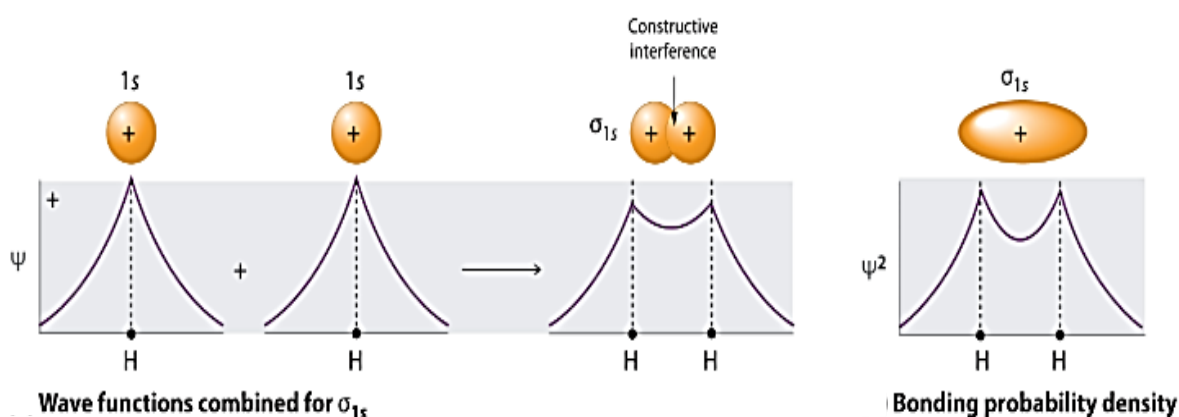


Figure 4.12: Bonding probability density.

4.4.1.2. Antibonding Molecular Orbital

The second possible combination between two 1s atomic orbitals is subtraction (**Fig. 4.13**). It is shown that the mathematical form of the antibonding molecular orbital is given by: $(1s_A - 1s_B)^2$, which gives:

$$(1s_A - 1s_B)^2 = 1s_A^2 + 1s_B^2 - 2 \times 1s_A 1s_B$$

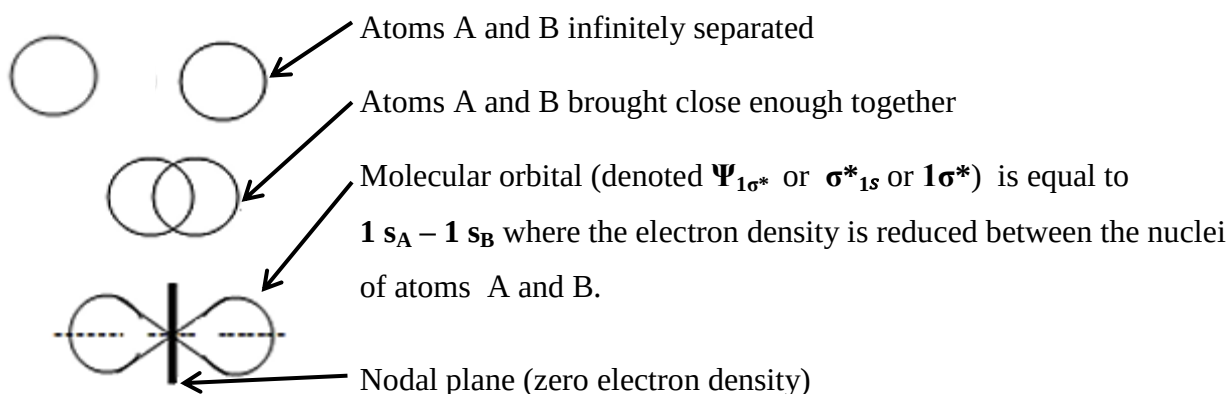


Figure 4.13: Antibonding molecular Orbital.

Antibonding σ^* orbital; $\Psi_{1\sigma^*} = \Psi_{1s_A} - \Psi_{1s_B}$

Such a subtraction reveals a node between the two nuclei (**Fig. 4.13**). This node implies both a wave function and an electron density that are zero.

It is also noted that the representation $(1s_A - 1s_B)^2$ shows a reduced electron density between the two nuclei. Indeed, the electrons are repelled away from the region between the two nuclei and cannot "cement" the two atoms. This results in strong repulsion between the two nuclei and an increase in the energy of the system (**Fig. 4.14**).

Therefore, the electrons will occupy an orbital whose energy is higher than that of the isolated atomic orbitals. This is called an **antibonding molecular orbital**.

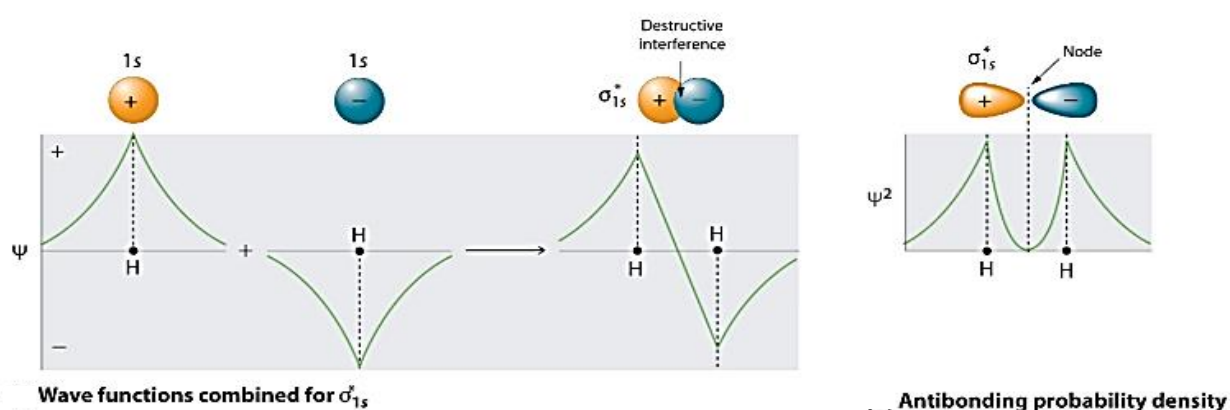


Figure 4.14: Antibonding probability density.

4.4.2. Formation and nature of bonds

4.4.2.1. Axial overlap

When two orbitals overlap axially, i.e. along the line joining the two nuclei, the bond is known as sigma (σ) bond and the orbitals are known as ' σ ' orbitals. Sigma bond is possible between two 's' orbitals or 's' and 'p' orbitals or 'p' and 'p' orbitals. A typical example of sigma bond is the bond formed in the formation of hydrogen molecule (**Fig. 4.15**).

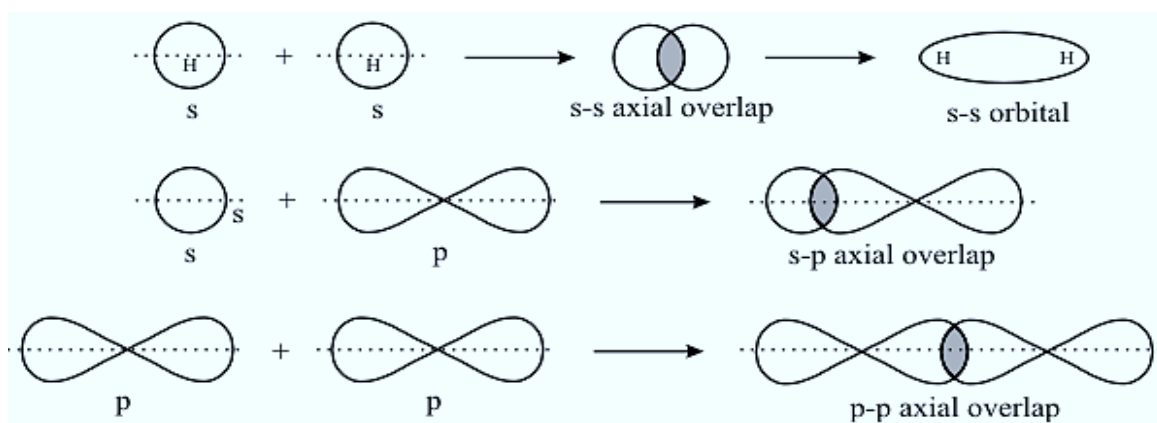


Figure 4.15: Formation of σ bond.

4.4.2.2. Lateral overlap

Molecular orbital formed by lateral overlapping of atomic orbitals is called π orbital and bond is known as Pi (π) bond. It consists of two parts, one electron cloud above and another below the axis line (**Fig.4.16**). In this, overlapping is less, therefore, p bond is weaker as compared to s bond. The multiple bonds of organic molecules are a combination of one sigma bond and one or two Pi bonds.

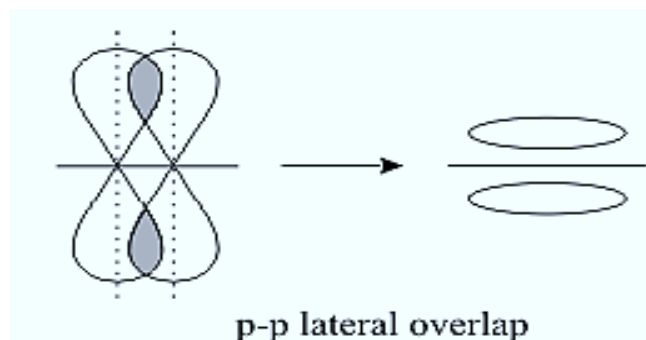


Figure 4.16: Formation of π bond.

4.4.3. Representation of the Molecular Orbital diagram

From two Atomic Orbitals of the same energy, two Molecular Orbitals are constructed: 1 bonding M.O. and 1 antibonding M.O. They are represented in the following relative energy diagram (**Fig. 4.17**).

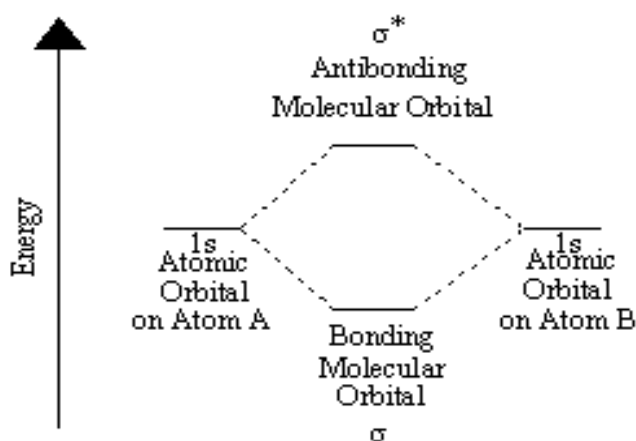


Figure 4.17: Molecular orbital energy diagram.

The Pauli principle, the stability principle, and Hund's rule are applicable to molecular orbitals.

It is therefore possible to write the electronic configuration of a homonuclear molecule A_2 or heteronuclear molecule AB .

- For $[2Z_A \text{ or } (Z_A + Z_B)] \geq 16$, we will have:



the energy of the MO σ_{2pz} is greater than that of $\pi_{2px,y}$.

- For $(Z_A + Z_B) < 16$, there will be an inversion of the MO: σ_{2pz} and $(\pi_{2px} = \pi_{2py})$, according to:



The inversion of the MOs is due to the fact that the difference between the atomic orbital levels 2s–2p is quite small. It is also said that there is an interaction between these orbitals, hence the inversion.

- **Bond order (BO)**

The number of bonds in a molecule, or the bond order (BO), is defined by the relation:

$$BO = \frac{1}{2} [(\text{number of bonding electrons}) - (\text{number of anti-bonding electrons})]$$

In MO theory, bond order is not just a counting rule (like in Lewis structures); it's a measure of the net number of bonding interactions.

- BO = 1 corresponds to a single bond (always a σ bond).
- BO = 2 corresponds to a double bond (consists of one σ bond and one π bond).
- BO = 3 corresponds to a triple bond (consists of one σ bond and two π bonds).
- BO = 0 means no bond exists.

Fractional BO is possible, which is a key advantage of MO theory.

- **Stability of molecules**

A higher bond order means a more stable molecule.

- BO > 0: A bond exists (e.g., H₂, O₂, N₂).
- BO = 0: No bond exists. The molecule is not stable (e.g., He₂).

- **Bond Strength**

A higher bond order corresponds to a stronger bond (more energy required to break it).

- **Bond Length**

A higher bond order corresponds to a shorter bond length.

- **Magnetic properties**

A molecule is said to be diamagnetic when it has no unpaired electrons.

A molecule is said to be paramagnetic when it has unpaired electrons.

4.4.3.1. Energy diagram of homonuclear diatomic molecules (symmetric)

- **H₂ molecule**

$${}_1\text{H} : 1s^1 \quad 2Z_{\text{H}} = 2 < 16$$

In molecular orbital theory, a bond is found in the H₂ molecule, just as in the classical bond theory (**Fig. 4.18**).

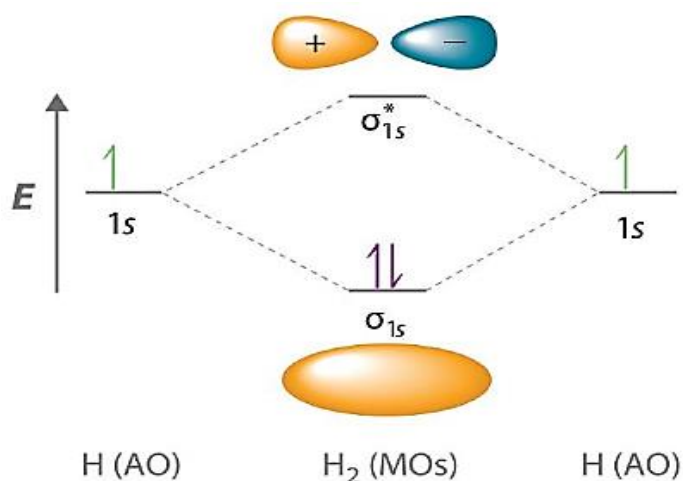


Figure 4.18: Energy diagram of the molecular orbitals for the H₂ molecule.

The electronic configuration of the MO is: σ_{1s}^2

The bond order $\text{BO} = \frac{1}{2} (2 - 0) = 1$ bond for the hydrogen molecule (1 σ bond).

There are no unpaired electrons → the H₂ molecule is **diamagnetic**.

- **He₂ molecule**

$${}_2\text{He} : 1s^2 \quad 2Z_{\text{He}} = 4 < 16$$

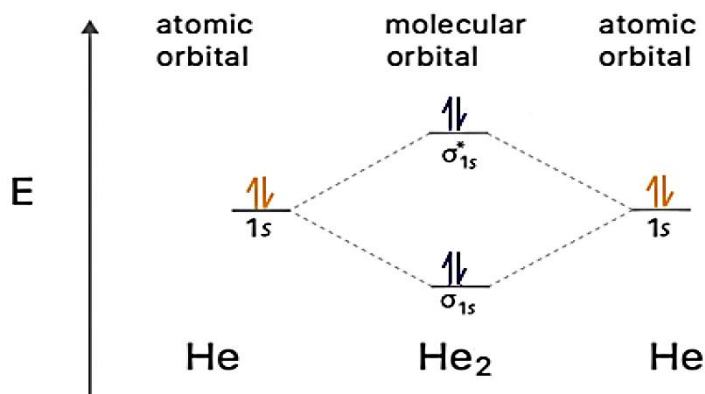


Figure 4.19: Energy diagram of the molecular orbitals for the He₂ molecule.

The electronic configuration of the MO is: $\sigma_{1s}^2 \sigma_{1s}^{*2}$ (**Fig. 4.19**).

The bond order $BO = \frac{1}{2} (2 - 2) = 0$

A bond order of 0 indicates that He_2 is not stable under normal conditions and does not form a chemical bond.

- **N_2 molecule**

${}_7\text{N} : 1s^2 2s^2 2p^3$ $2Z_{\text{N}} = 14 < 16$ (inversion of MO, **Fig 4.20**)

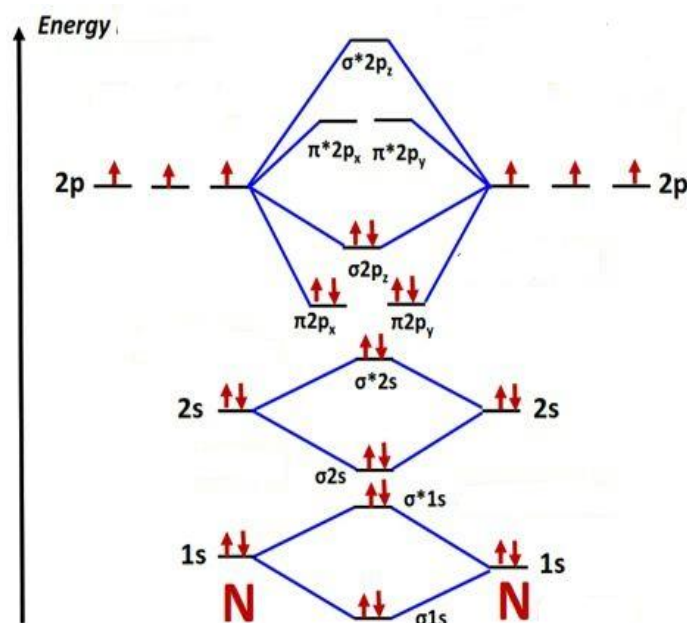


Figure 4.20: Energy diagram of the molecular orbitals for the N_2 molecule.

The electronic configuration of the MO is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2$.

$BO = \frac{1}{2} (8 - 2) = 3$ bonds (1 σ bond and 2 π bonds).

There are no unpaired electrons $\rightarrow$ the N_2 molecule is **diamagnetic**.

- **O_2 molecule**

${}_8\text{O} : 1s^2 2s^2 2p^4$ $2Z_{\text{O}} = 16$ (no inversion of MO, **Fig 4.21**)

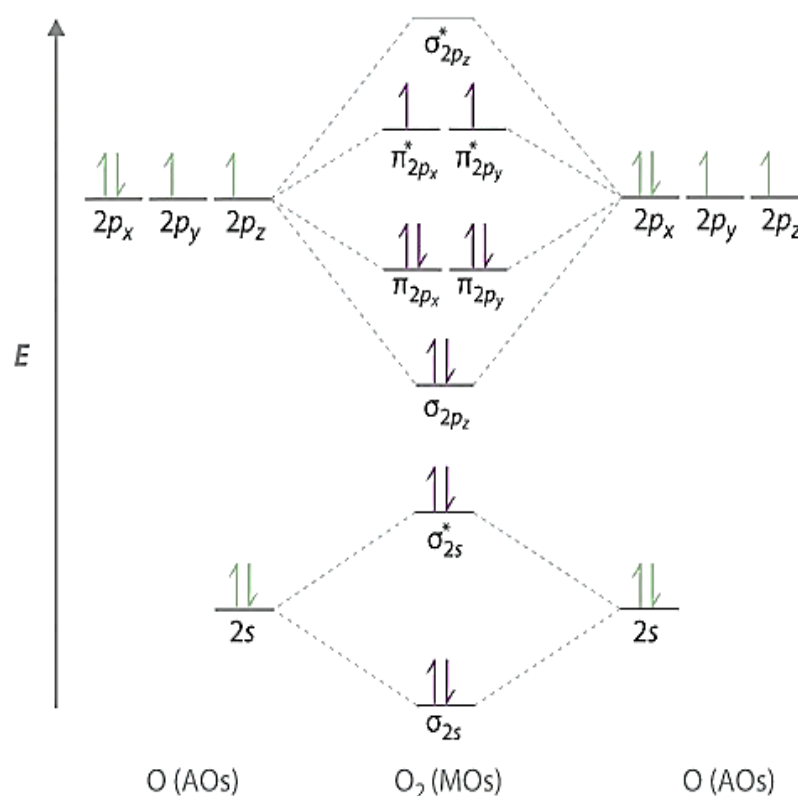


Figure 4.21: Energy diagram of the molecular orbitals for the O₂ molecule.

The electronic configuration of the MO is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \pi_{2px}^2 \pi_{2py}^2 \pi_{2px}^{*1} \pi_{2py}^{*1}$

BO = $\frac{1}{2} (8 - 4) = 2$ bonds (1 σ bond and 1 π bond).

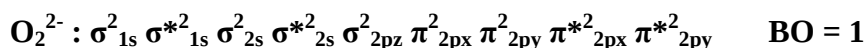
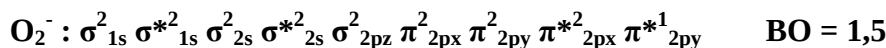
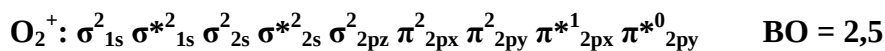
There are unpaired electrons $\rightarrow$ the O₂ molecule is **paramagnetic**.

Exercise

Arrange the following four molecular oxygen species in order of increasing bond length: O₂⁺, O₂, O₂⁻, and O₂²⁻.

Correction

The electron configurations for the four species are contrasted below.



The bond order decreases and the bond length increases in the order. The predicted order of increasing bond length then is O₂⁺ < O₂ < O₂⁻ < O₂²⁻.

This trend is confirmed experimentally with O^+_2 (112.2 pm), O_2 (121 pm), O^-_2 (128 pm) and O^{2-}_2 (149 pm).

4.4.3.2. Energy diagram of heteronuclear diatomic molecules (asymmetric)

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two non-identical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a “skewed” molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in **Figure 4.22**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

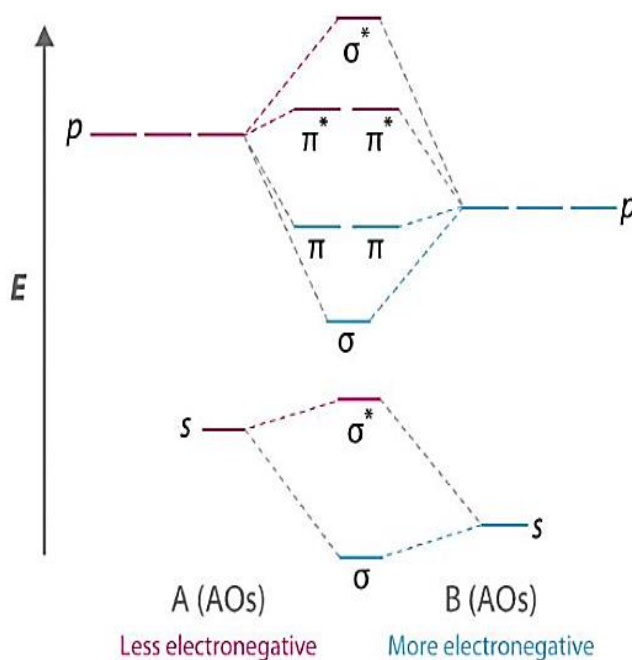
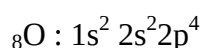
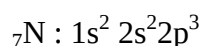


Figure 4.22: Energy diagram of heteronuclear diatomic molecules

Example

NO molecule



$Z_N + Z_O = 15 < 16$ (inversion of MO, **Fig 4.23**).

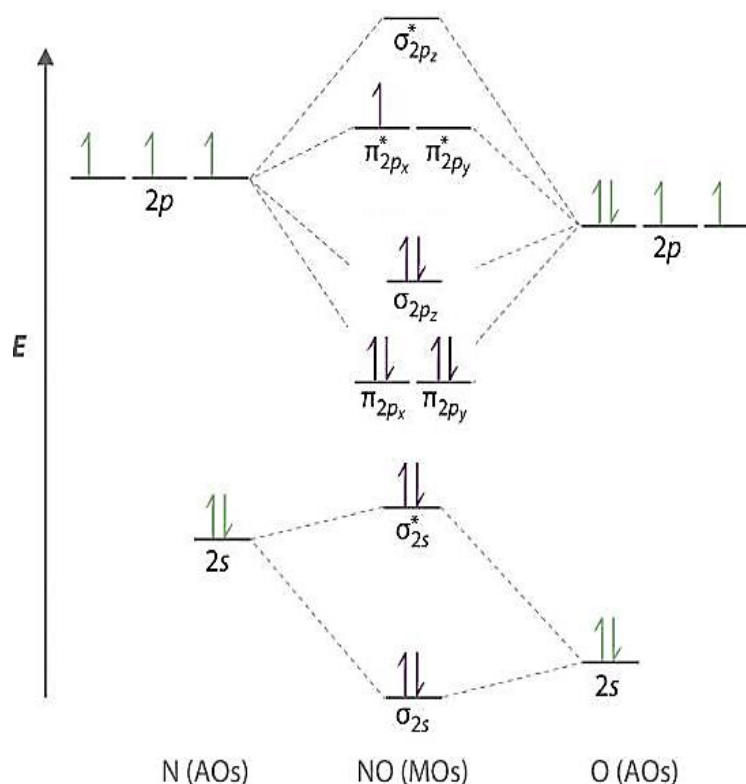


Figure 4.23: Energy diagram of the molecular orbitals for the NO molecule.

The electronic configuration of the MO is: $\sigma^2_{1s} \sigma^{*2}_{1s} \sigma^2_{2s} \sigma^{*2}_{2s} \pi^2_{2px} \pi^2_{2py} \sigma^2_{2pz} \pi^{*1}_{2px}$

$BO = \frac{1}{2} (8 - 3) = 2,5$ bonds

There are unpaired electrons $\rightarrow$ the NO molecule is **paramagnetic**.

4.4.4. Polyatomic molecules - atomic orbital hybridization theory

Hybridization is a model used to explain how atomic orbitals mix to form new, identical hybrid orbitals suitable for the geometric arrangements of atoms in molecules. The central atom is usually the one we focus on.

The main types of hybridization are:

- sp^3 Hybridization
- sp^2 Hybridization
- sp Hybridization
- Other types (like sp^3d , sp^3d^2 for expanded octets)

Here is a quick comparison of the most common types (**Table 4.2**).

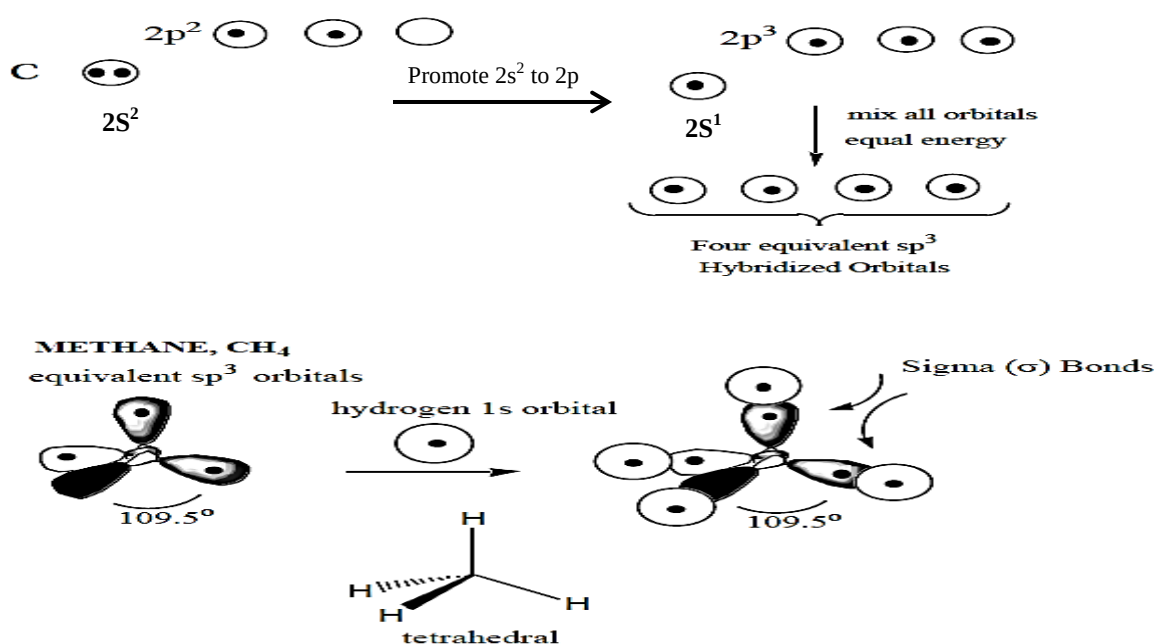
Table 4.2: Different types of hybridization

Hybridization Type	Orbitals Mixed	Geometry	Bond Angle	Example
sp^3	One s + Three p	Tetrahedral	$\sim 109.5^\circ$	CH_4 (Methane)
sp^2	One s + Two p	Trigonal Planar	$\sim 120^\circ$	C_2H_4 (Ethene)
sp	One s + One p	Linear	180°	C_2H_2 (Acetylene)

4.4.4.1. sp^3 hybridization Tetrahedral (tetragonal)

In carbon ($1s^2 2s^2 2p^2$) one of the electrons of the $2s^2$ orbital is promoted to the third $2p^0$ orbital. The s and three p orbitals hybridize to form four new orbitals of equal energy called sp^3 hybrid orbitals. The electrons in the four sp^3 hybridized orbitals bond by overlap with the $1s^1$ hydrogen orbital. The single covalent bond is called a **sigma (σ)** bond.

The arrangement is tetrahedral with a bond angle of $109,5^\circ$ (Fig. 4.24)

Figure 4.24: sp^3 hybridization.

The unique property of carbon that differentiates it from the other elements and allows the formation of so many different organic compounds is the ability of carbon to bond with itself through covalent bonding. Thus, addition of another carbon atom to methane results in ethane which has covalent sigma bonds to the hydrogen atoms and a covalent sigma bond between the carbon atoms (Fig. 4.25).

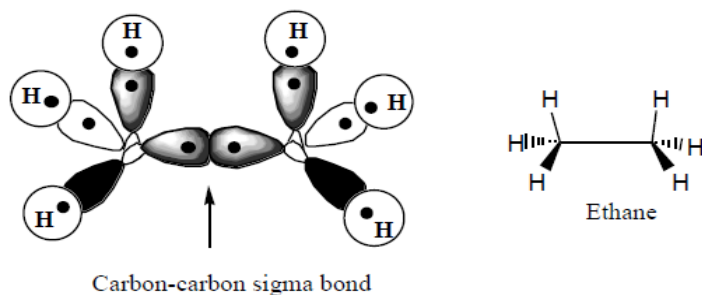


Figure 4.25: Formation of ethane molecule.

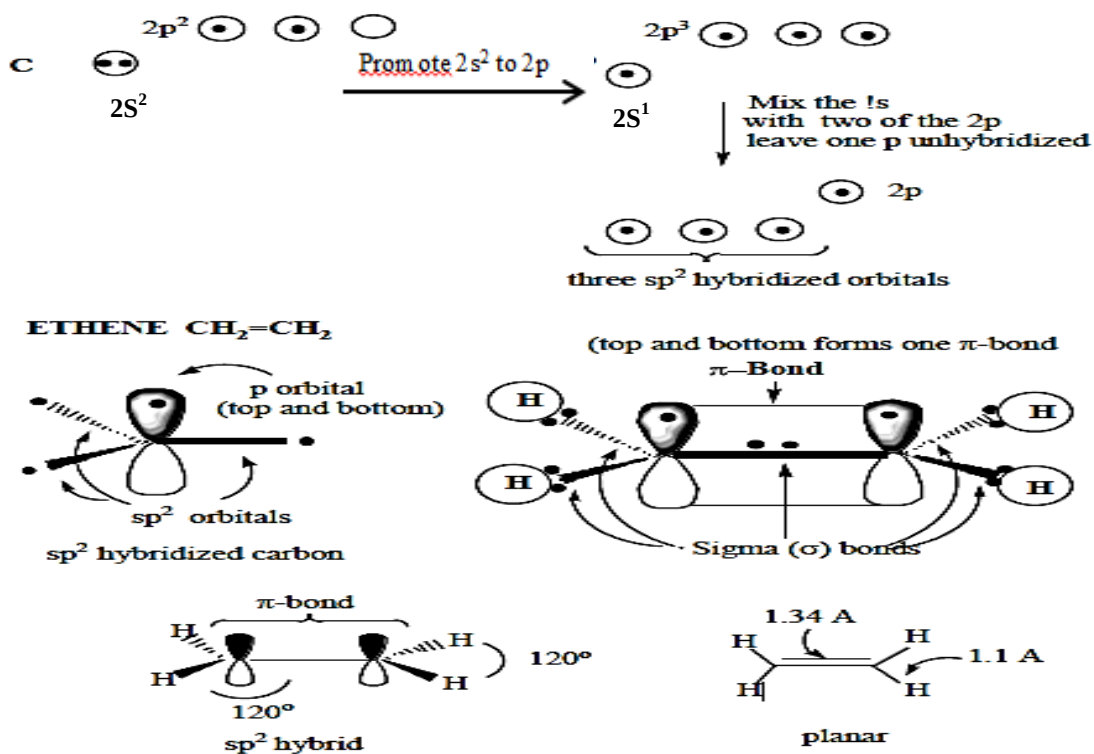
4.4.4.2. sp^2 hybridisation (trigonal)

The sp^2 hybridization occurs when the s orbital is mixed with only two p orbitals. So, three orbitals are mixed, and the outcome is three hybrid orbitals which are called sp^2 hybrid orbitals.

1 s orbital + 2 p orbitals $\longrightarrow$ 3 sp^2 hybrid orbitals + 1 pure p orbital

The combination of two of the sp^2 hybridized carbon atom leads to two carbon atoms being joined by overlap of sp^2 orbitals to form a C-C single bond, and the side-to-side overlap of the p orbitals to form another bond known as a pi (π) bond (Fig. 4.26).

The bonding in an ethene, the molecule is planar with bond angles of 120° and a C=C bond length that is longer than the C-H bond length.

Figure 4.26: sp^2 hybridization.

4.4.4.3. sp hybridization or digonal

In sp hybridization, the s orbital of the excited state carbon is mixed with only one out of the three 2p orbitals. The new orbitals formed are called **sp hybridized orbitals**. It forms linear molecules with an angle of 180° (**Fig. 4.27**).

$1\text{ s orbital} + 1\text{ p orbital} \longrightarrow 2\text{ sp hybrid orbitals} + 2\text{ pure p orbitals}$

The simplest molecule associating 2 sp hybridized carbons is that of acetylene.

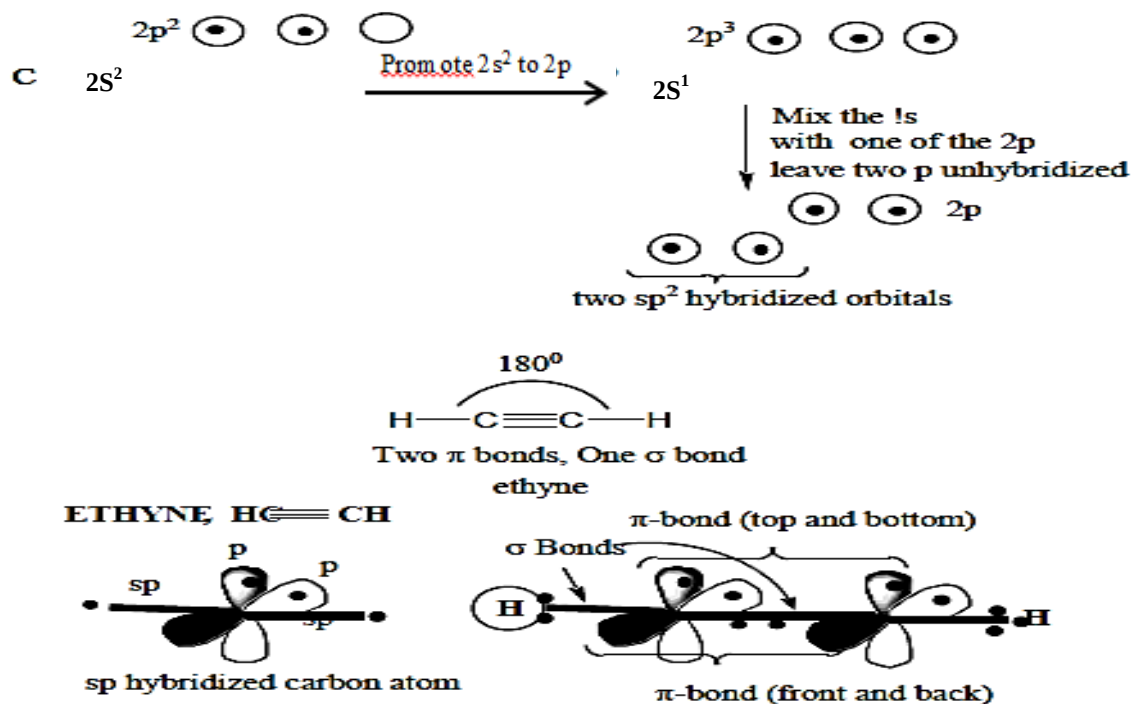
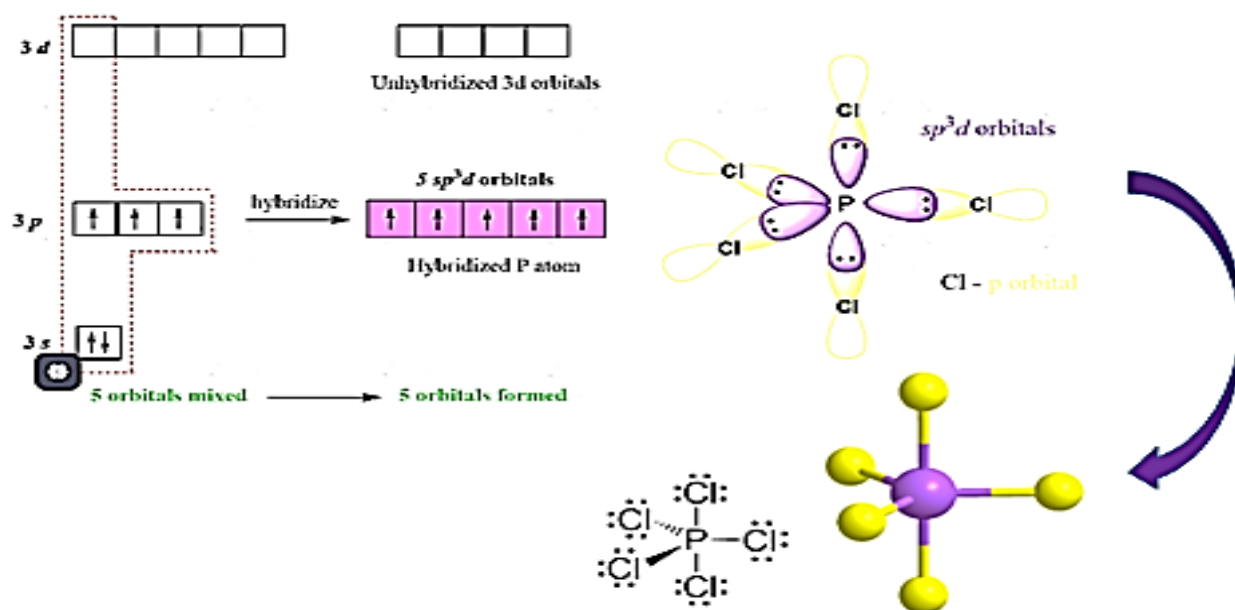


Figure 4.27: sp hybridization.

4.4.4.4. sp^3d hybridization

The elements capable of adopting trigonal bipyramidal or octahedral geometry must be in period 3 or higher, because d orbitals are needed to produce five or more hybrid orbitals. For example, the electron configuration of phosphorous is: P: $1s^2 2s^2 2p^6 3s^2 3p^3$.

And in addition to the 3s and 3p orbitals, it also has the five 3d orbitals available for hybridization. The five half-filled sp^3d orbitals are formed by mixing one s (the 3s orbital), three p (the 3p orbitals), and one d (one 3d orbital). Four 3d orbitals are left unhybridized and empty. Each of the sp^3d orbitals makes a bond with the p orbital of chlorine forming a trigonal bipyramidal geometry (**Fig. 4.28**).

Figure 4.28: sp^3d hybridization.

4.4.4.5. sp^3d^2 hybridization

Let's consider the structure of sulfur hexafluoride, SF_6 . The central atom has six atoms connected, and therefore, it needs six equivalent orbitals, which is achieved by the sp^3d^2 hybridization. The electron configuration of sulfur is: S : $1s^2 2s^2 2p^6 3s^2 3p^4$. There are two d orbitals mixed with the s and p orbitals thus making six hybrid orbitals each hosting one electron.

There are six sp^3d^2 half-filled orbitals of the s atom and each overlaps with a half-filled 2p orbital of an F atom. As for the geometry, the central atom has 6 atoms connected to it, and no lone pairs, therefore, the geometry is octahedral (Fig. 4.29).

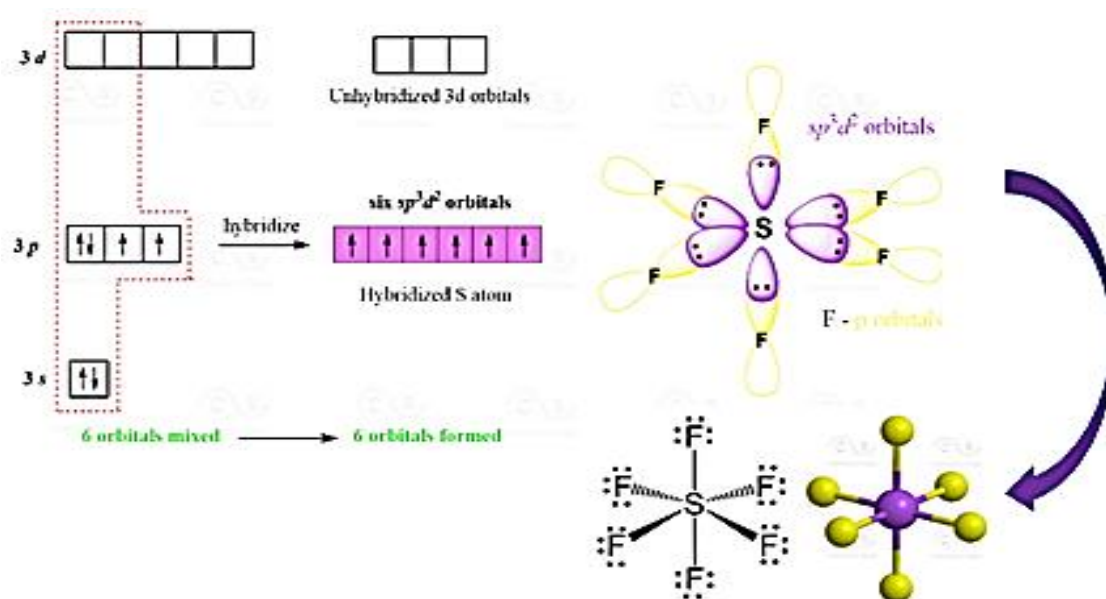


Figure 4.29: sp^3d^2 hybridization.

Exercises

Exercise 1

1. Represent the following elements from the periodic table using the Lewis model:
H, He, Be, B, C, N, O, P, S, Cl.
2. Provide the Lewis notation for the following molecules and ions: CO_2 ; CO_3^{2-} ; HClO_4 ; POCl_3 ; SO_2 ; N_2H_2 .
3. Based on the electronic structures of sulfur and phosphorus atoms, explain the formation of the SF_6 and PCl_5 molecules.
4. Predict the possible valences of phosphorus. The two chlorides PCl_3 and PCl_5 exist. Explain why only NCl_3 is known, while NCl_5 does not exist.

Exercise 2

The measured dipole moment of hydrogen fluoride (HF) is 1,82 D. Given that the covalent radius of H and F are 0,037 nm and 0,064 nm, respectively.

1. What is the value of the partial charges δ located on H and F?
2. What is the percentage of ionicity (% ionic character) of the HF bond?

Given: 1 Debye = $0,33 \times 10^{-29}$ C.m.

Exercise 3

The dipole moment of hydrogen sulfide H_2S is 0,95 Debye. The bond angle between the S-H bonds is 95° . Calculate:

1. The dipole moment of the S-H bond in this molecule.
2. The partial ionic character of this bond, given that the S-H bond length is 1,3 Å.

Exercise 4

1. Provide the energy level diagram of the molecular orbitals (MOs) for the N_2 molecule and CN.
2. Deduce 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^+ .

Exercise 5

1. Provide the energy level diagram of the molecular orbital (MO) for the heteronuclear molecule CO.
2. Deduce the electron configurations of CO; CO⁺ and CO⁻ and their bond order.
3. Which of these species has the shortest bond?
4. Indicate their magnetic property.

Exercise 6

Complete the following table. Given: ${}_6\text{C}$, ${}_7\text{N}$, ${}_8\text{O}$, ${}_{16}\text{S}$, ${}_{17}\text{Cl}$.

Chemical Species	Lewis Structure	Hybridization of the Central Atom	AX _m E _n	Geometry
OCS				
SO ₄ ²⁻				
SO ₃				
NOCl				
NO ₃ ⁻				

Correction

Exercise 1

1. Lewis notation for the element:

H (Z = 1) : $\underline{1s^1}$

He (Z = 2) : $\underline{1s^2}$

Be (Z = 4) : $\underline{1s^2} \underline{2s^2}$

B (Z = 5) : $\underline{1s^2} \underline{2s^2} \underline{2p^1}$

C (Z = 6) : $\underline{1s^2} \underline{2s^2} \underline{2p^2}$

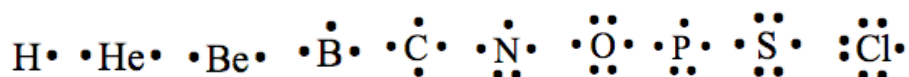
N (Z = 7) : $\underline{1s^2} \underline{2s^2} \underline{2p^3}$

O (Z = 8) : $\underline{1s^2} \underline{2s^2} \underline{2p^4}$

P (Z = 15) : $\underline{1s^2} \underline{2s^2} \underline{2p^6} \underline{3s^2} \underline{3p^3}$

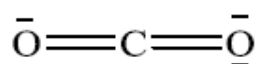
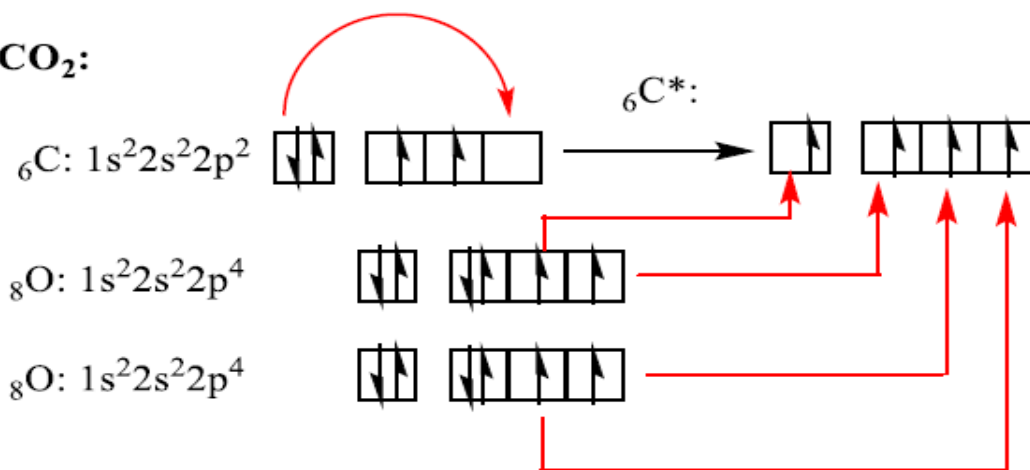
S (Z = 16) : $\underline{1s^2} \underline{2s^2} \underline{2p^6} \underline{3s^2} \underline{3p^4}$

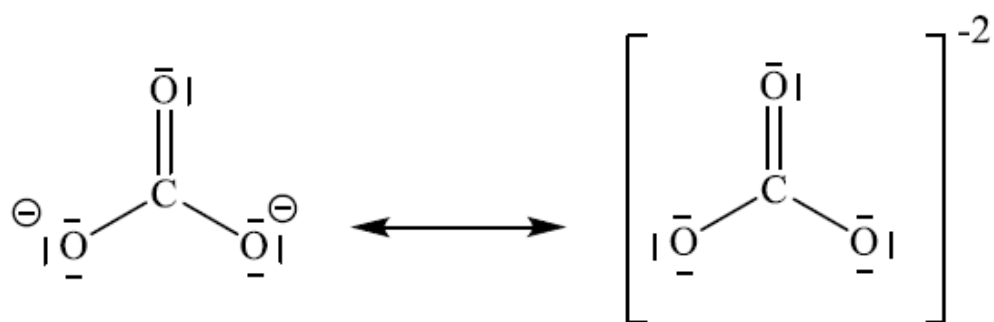
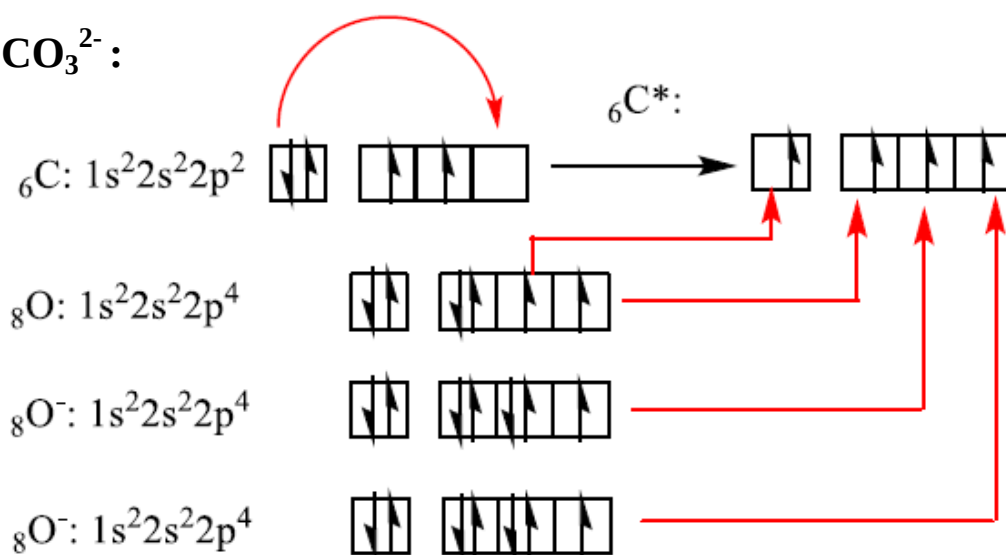
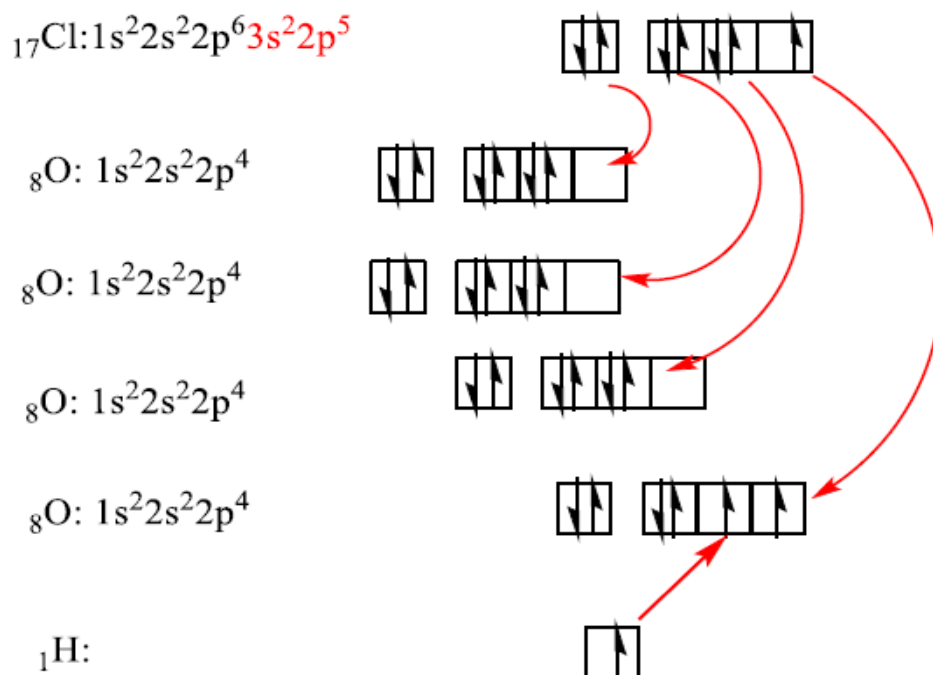
Cl (Z = 17) : $\underline{1s^2} \underline{2s^2} \underline{2p^6} \underline{3s^2} \underline{3p^5}$

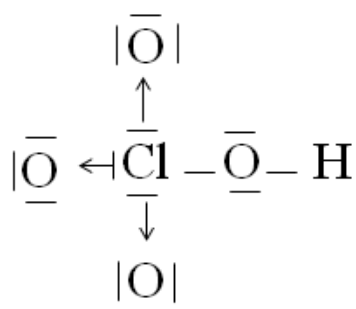
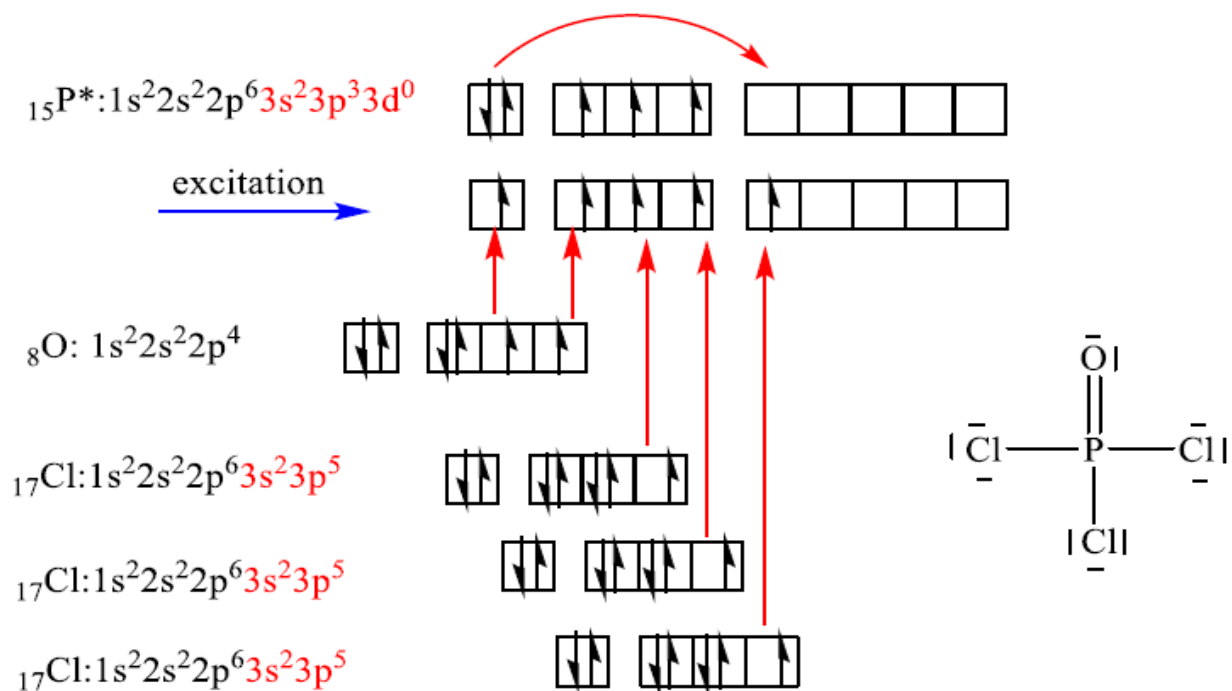
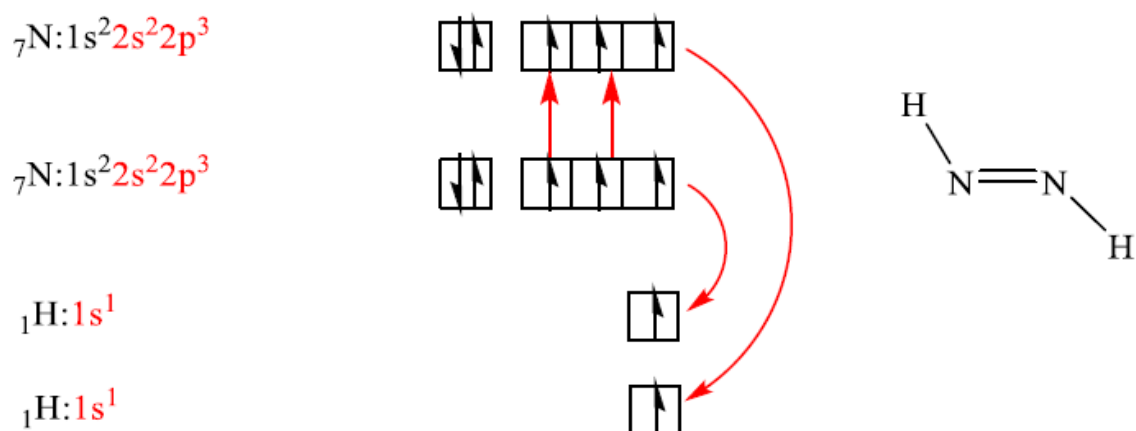


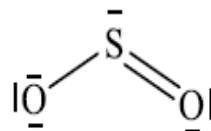
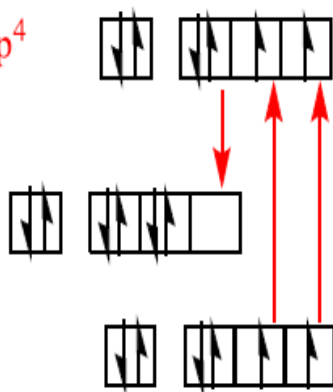
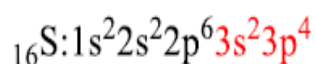
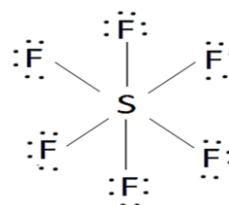
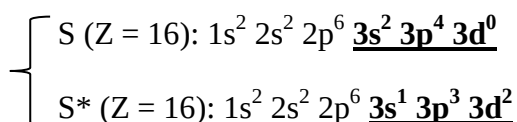
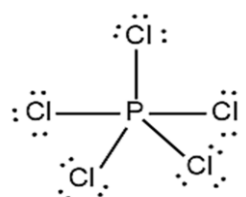
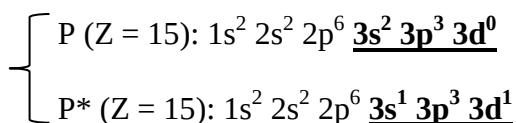
2. Lewis notation for the following molecules and ions:

CO₂:



CO_3^{2-} : HClO_4 :

**POCl₃:****N₂H₂:**

SO₂:3. Formation of SF₆ and PCl₅ molecules.**6 unpaired electrons****5 unpaired electrons**

Sulfur and phosphorus are atoms from the 3rd period. Therefore, they can accommodate more than 8 electrons by using the 3d atomic orbitals.

4. In nitrogen and phosphorus, the number of outer electrons is 5, with 3 unpaired electrons; hence the existence of NCl₃ and PCl₅.

The formation of PCl₅ involves 5 unpaired electrons distributed among the 3s, 3p, and 3d subshells. However, in the outer shell of nitrogen (n = 2; L shell), the d subshell does not exist.

Exercise 2

1. Calculation of partial charges δ on H and F

The dipole moment μ is given by: $\mu = q \times d = \delta \times e \times d$

Where:

δ is the partial charge

e is the elementary charge ($1,602 \times 10^{-19}$ C)

d is the bond length (in meters)

$$\mu = 1,82 \times 0,33 \times 10^{-29} = 6,006 \times 10^{-30} \text{ C.m}$$

Calculate bond length

d = covalent radius of H + covalent radius of F

$$d = 0,037 + 0,064 = 0,101 = 1,01 \times 10^{-10} \text{ m}$$

$$\text{Calculate } \delta = \mu / (e \times d) = (6,006 \times 10^{-30}) / (1,602 \times 10^{-19} \times 1,01 \times 10^{-10}) = 0.371$$

Therefore, the partial charge on H is + 0,371 and on F is - 0,371.

2. Calculation of percentage ionicity of HF bond

The percentage ionicity is given by: % ionicity = **P.I.C** = $\frac{\mu_{\text{Experimental}}}{\mu_{\text{theoretical}}} \times 100$

$$\text{Calculate } \mu_{\text{Theoretical}} = e \times d = 1,602 \times 10^{-19} \times 1,01 \times 10^{-10} = 1.618 \times 10^{-29} \text{ C.m}$$

$$\text{Calculate PIC} = (6,006 \times 10^{-30} / 1,618 \times 10^{-29}) \times 100 = 0.371 \times 100 = 37.1\%$$

Therefore, the percentage ionic character of the HF bond is 37,1%.

Exercise 3

Dipole Moment of the S–H Bond in a bent molecule like H₂S, the total dipole moment is the vector sum of the two bond dipole moments. If each bond has a dipole moment $\mu_{\text{S-H}}$, and the bond angle is θ , then:

$$\mu_{\text{H}_2\text{S}} = 2 \times \mu_{\text{S-H}} \times \cos(\theta/2)$$

$$\mu_{\text{S-H}} = \mu_{\text{H}_2\text{S}} / (2 \times \cos(\theta/2)) = 0,95 / (2 \times \cos 47,5) = 0.70 \text{ D}$$

2. Partial ionic character of the S–H Bond

The ionic character is given by:

$$\text{P.I.C} = \frac{\mu_{\text{Experimental}}}{\mu_{\text{theoretical}}} \times 100$$

$$\mu_{\text{Theoretical}} = e \times d = 1.602 \times 10^{-19} \times 1.3 \times 10^{-10} = 2,0826 \times 10^{-29} = 6,31 \text{ D}$$

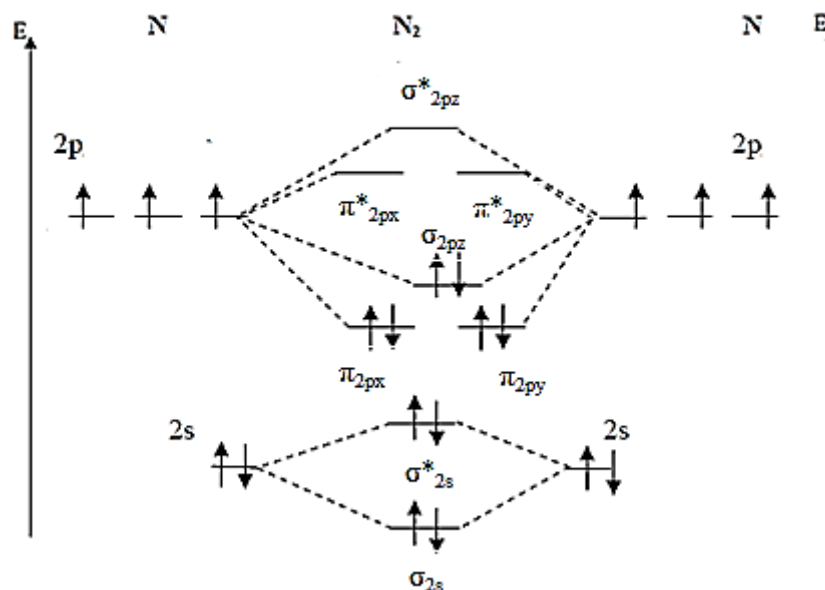
$$\text{PIC} = (0,7/6,31) \times 100 = 11,09 \%$$

Exercise 4

1. Molecular orbital (MO) energy diagram of the homonuclear N₂ molecule: (N: Z=7)

There are interactions between the s and p atomic orbitals which involve an inversion of the π_x and π_y molecular orbitals with the σ_{pz} molecular orbital.

$$\text{N (Z = 7): } 1s^2 2s^2 2p^3$$

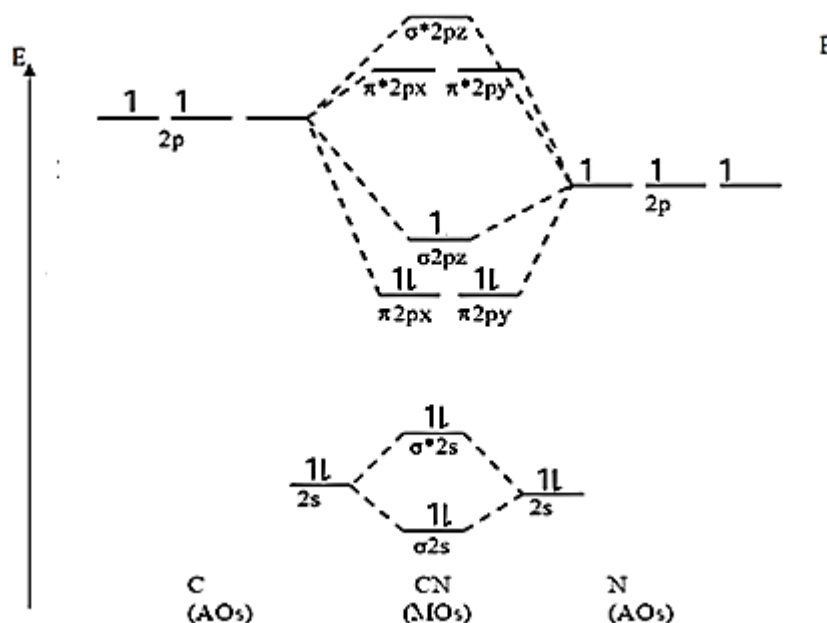


The electronic configuration of the MO is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2$.

2. Molecular Orbital (MO) Energy Diagram of the Heteronuclear CN Molecule:

For heteronuclear molecules formed from atoms in the second period of the periodic table, there are interactions between the s and p atomic orbitals which involve an inversion of the π_x and π_y molecular orbitals with the σ_{pz} molecular orbital.

N ($Z = 7$) : $1s^2 2s^2 2p^3$ C ($Z = 6$) : $1s^2 2s^2 2p^2$



The electronic configuration of the MO is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^1$.

2. Magnetic properties of N_2 and CN.

The presence of an unpaired electron in the molecular orbitals of CN makes this molecule paramagnetic.

In contrast, in the N_2 molecule, we find that the electrons are paired; this gives N_2 a diamagnetic character.

$$3. \text{BO}(N_2) = \frac{1}{2}(8-2) = 3$$

$$\text{BO}(N_2^+) = \frac{1}{2}(7-2) = 2,5$$

$$\text{BO}(\text{CN}) = \frac{1}{2}(7-2) = 2,5$$

$$\text{BO}(\text{CN}^-) = \frac{1}{2}(8-2) = 3$$

When the bond order decreases, the bond length increases, the interaction weakens, the bond strength becomes less intense, and the dissociation energy ΔH_d decreases:

$$\text{BO}(N_2^+) < \text{BO}(N_2) \rightarrow \Delta H_d(N_2^+) < \Delta H_d(N_2)$$

N_2^+ is less stable than N_2

$$\text{BO}(\text{CN}) < \text{BO}(\text{CN}^-) \rightarrow \Delta H_d(\text{CN}) < \Delta H_d(\text{CN}^-)$$

CN is less stable than CN^-

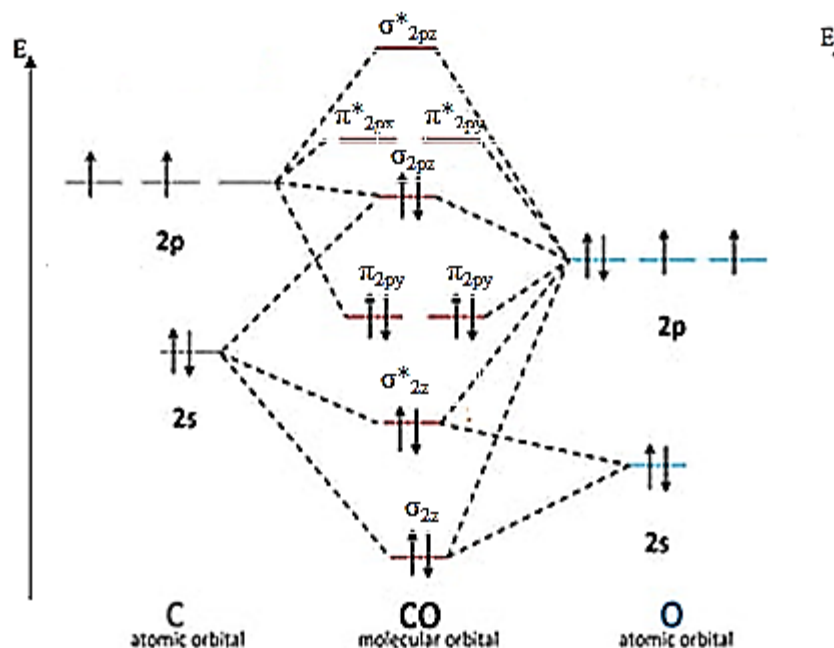
Exercise 5**1. Energy diagram of the molecular orbital (MO) of the CO molecule:**

For heteronuclear molecules formed from atoms of the second period of the periodic table, there are interactions between the s and p atomic orbitals which involve an inversion of the π_x and π_y molecular orbitals with the σ_{pz} molecular orbital.

$$\text{C} (Z = 6) : 1s^2 2s^2 2p^2$$

$$\text{O} (Z = 8) : 1s^2 2s^2 2p^4$$

The oxygen atom (O) is more electronegative than the carbon atom. Therefore, the energies of the atomic orbitals of oxygen are lower than those of carbon. In this case, the energy diagram is asymmetric.



2. The electronic configurations of CO, CO⁺, CO⁻

The electronic configuration of CO is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2$.

The electronic configuration of CO⁺ is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^1$.

The electronic configuration of CO⁻ is: $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2 \pi_{2px}^{*1}$.

The bond orders are:

$$\text{BO (CO)} = \frac{1}{2}(8-2) = 3$$

$$\text{BO (CO}^+) = \frac{1}{2}(7-2) = 2,5$$

$$\text{BO (CO}^-) = \frac{1}{2}(8-3) = 2,5$$

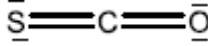
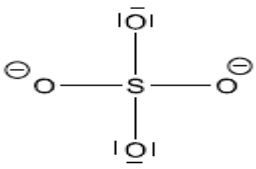
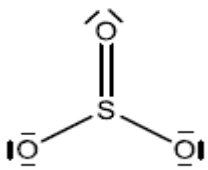
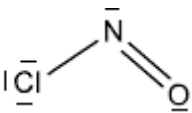
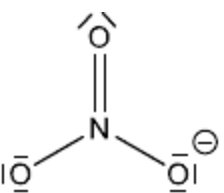
3. The greater the bond order (BO), the smaller the bond length (d). The order of bond length is:

$$d(\text{CO}^-) = d(\text{CO}^+) < d(\text{CO})$$

4. The presence of an unpaired electron in the molecular orbitals of CO⁻ and CO⁺ makes these molecules paramagnetic.

In contrast, in the CO molecule, the electrons are all paired, which gives CO a diamagnetic character.

Exercise 6

Chemical Species	Lewis Structure	Hybridization of the Central Atom	AX_mE_n	Geometry
OCS		sp	AX_2	Linear
SO_4^{2-}		sp^3	AX_4	Tetrahedral
SO_3		sp^2	AX_3	Trigonal Planar
NOCl		sp^2	AX_2E	Bent
NO_3^-		sp^2	AX_3	Trigonal Planar

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**EXTRAIT DU PV
DE LA REUNION ORDINAIRE DU CONSEIL SCIENTIFIQUE
Du 02/02/2026**

Objet : : Expertise de polycopié pédagogique

En l'an deux mille vingt-six (2026), le lundi 02 février à 13 h 30, une réunion ordinaire du Conseil Scientifique de la Faculté des Sciences de la Matière et de l'Informatique s'est tenue dans la salle de réunion de la faculté (Bloc B).

Suite aux rapports favorables reçus de la part des experts cités ci-après concernant l'expertise du polycopié pédagogique, le CSF a prononcé favorablement pour la conformité du polycopié pédagogique en vue de préparer son habilitation.

- **Auteur du polycopié :** Dr. CHERIFI Souad (MCB)
- **Intitulé du polycopié :** Chemistry 1(Course and Exercises)
- **Destiné aux étudiants de :** 1ère année Licence Sciences de la Matière.
- **Experts du polycopié :**

- | | | |
|-----------------------|-----|--------------------|
| • BOUKHATEM Houria | MCA | UDB-Khemis Miliana |
| • DJAFER Abderrahmane | Pr | UHB- Chlef. |

Président du
Conseil Scientifique de la Faculté SMI
Dr. BOUDERBALA Miloud
المجلس العلمي
كلية علوم المادة والإعلام الآلي
بدر بلة ميهوب