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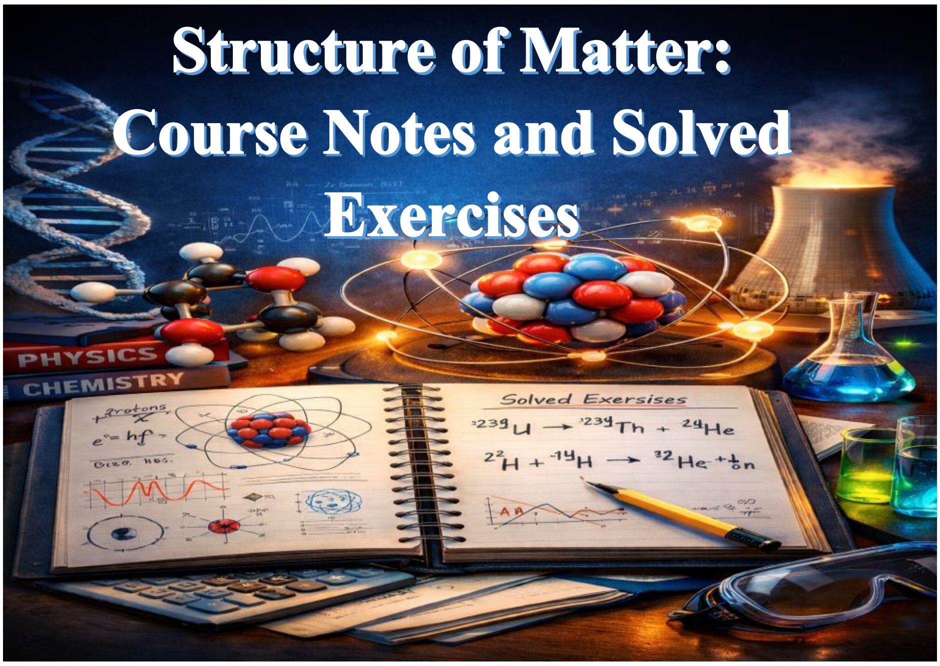

Structure of Matter: Course Notes and Solved Exercises

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Academic Year: 2024/2025

Syllabus

Semester: 1
Teaching Unit: UEF 1.1
Subject 3: Structure of Matter
Total Hours (VHS): 67h30 (Lectures: 3h00, Tutorials: 1h30)
Credits: 6
Coefficient: 3

Recommended Prerequisites:
Basic knowledge of mathematics and general chemistry.

Course Content:

Chapter 1: Fundamental Concepts (2 Weeks)

States and macroscopic characteristics of matter, phase changes of matter, concepts of atom, molecule, mole, and Avogadro's number, atomic mass unit, atomic and molecular molar mass, molar volume, Law of Conservation of Mass (Lavoisier), chemical reactions, qualitative and quantitative aspects of matter.

Chapter 2: Main Constituents of Matter (3 Weeks)

Introduction: Faraday's experiment – relationship between matter and electricity, evidence of the constituents of matter and of the atom, some physical properties (mass and charge), Rutherford's planetary model, presentation and characteristics of the atom (symbol, atomic number Z, mass number A, number of protons, neutrons, and electrons), isotopy and relative abundance of different isotopes, isotope separation and determination of atomic mass and average atomic mass: mass spectrometry (Bainbridge spectrograph), nuclear binding and cohesion energy, nuclear stability.

Chapter 3: Radioactivity – Nuclear Reactions (2 Weeks)

Natural radioactivity (α, β, and γ radiation), artificial radioactivity and nuclear reactions, kinetics of radioactive decay, applications of radioactivity.

Chapter 4: Electronic Structure of the Atom (2 Weeks)

Wave-particle duality, interaction between light and matter, Bohr's atomic model (hydrogen atom), the hydrogen atom in wave mechanics, multi-electron atoms in wave mechanics.

Chapter 5: Periodic Classification of Elements (3 Weeks)

Mendeleev's periodic classification, modern periodic classification, evolution and periodicity of physico-chemical properties of elements, calculation of radii (atomic and ionic), successive ionization energies, electron affinity and electronegativity (Mulliken scale) using Slater's rules.

Chapter 6: Chemical Bonding (3 Weeks)

Covalent bonding in Lewis theory, polar covalent bonds, dipole moment and partial ionic character of bonds, molecular geometry: Gillespie's theory (VSEPR), chemical bonding in the quantum model.

Assessment Method:
Continuous assessment: 40%; Final exam: 60%.

Foreword

The course material for *"Structure of Matter"* has been meticulously developed to offer students a comprehensive understanding of the core principles that govern the structure and behavior of matter at both macroscopic and atomic levels. This course is designed to build a strong foundation in the fundamental concepts of chemistry, which are essential for advanced studies in materials science, industrial engineering, and related fields.

In **Chapter 1**, the course introduces **fundamental concepts of matter**, covering essential topics such as the macroscopic properties of different states of matter, phase transitions, and the atomic and molecular foundations of chemical reactions. The chapter emphasizes the law of conservation of mass and provides a qualitative and quantitative framework for understanding matter.

Chapter 2 delves into the **constituents of matter**, examining the atomic structure, experimental methods for identifying atomic components, and the significance of isotopes. The chapter also discusses the principles of mass spectrometry and nuclear stability, providing a crucial understanding of the atomic model and its applications. **Chapter 3** explores **radioactivity and nuclear reactions**, analyzing both natural and artificial radioactivity. It provides an in-depth examination of radioactive decay kinetics and their applications in various scientific domains, including medicine and energy production. **Chapter 4** focuses on the **electronic structure of the atom**, incorporating the wave-particle duality, the interaction of light and matter, and the quantum mechanical model of the atom. This chapter offers a deeper understanding of atomic and molecular behavior, integrating both classical and modern theories.

Chapter 5 presents the **periodic classification of elements**, from Mendeleev's original periodic table to the modern quantum-based classification. This chapter explains periodic trends in atomic properties, providing students with the tools to predict chemical reactivity and behavior.

Finally, **Chapter 6** investigates **chemical bonding**, including covalent bonds, molecular geometry, and the quantum mechanical treatment of chemical interactions. This chapter presents a thorough examination of how atoms combine to form stable molecules, essential for understanding complex chemical reactions.

The accompanying **solved exercises** aim to reinforce theoretical knowledge through practical application, allowing students to apply their understanding to real-world chemical problems.

These exercises are carefully selected to challenge students and encourage independent critical thinking.

This material aims to not only provide a detailed understanding of the structure of matter but also to inspire further academic exploration in the field of chemistry and materials science. It is my hope that students will engage with these concepts rigorously, as they lay the groundwork for future research and innovations in both theoretical and applied chemistry.

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Chapter I: Fundamental Concepts

1. Introduction

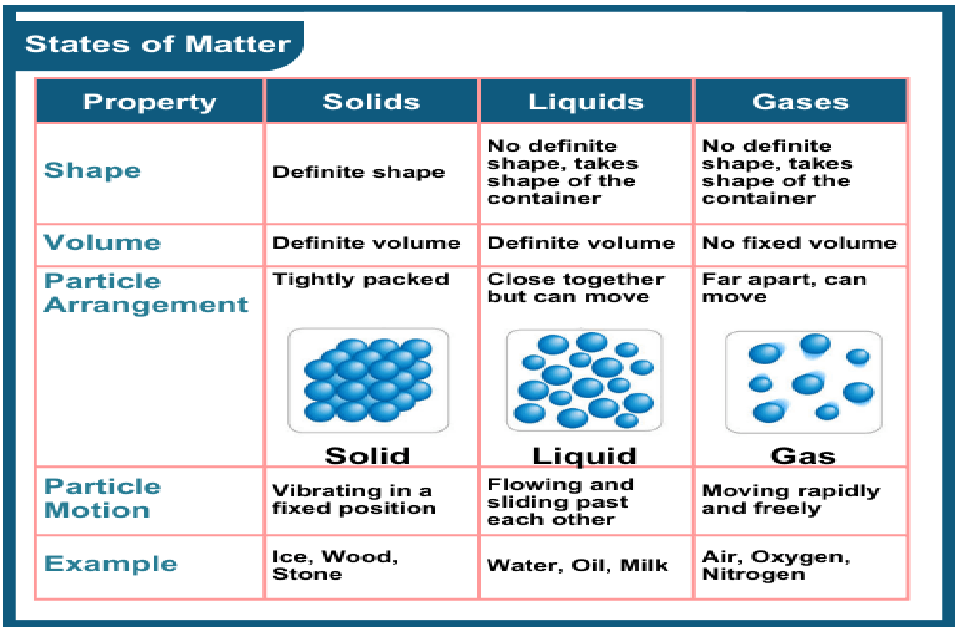
Chemistry is an experimental science that studies the various atomic and molecular constituents, the properties of crystallizable or volatile objects, whether natural or artificial, and the laws governing the phenomena of combination or decomposition resulting from their molecular interactions with each other.

- ✓ Matter is omnipresent in our surroundings.
- ✓ It is discontinuous in nature, composed of elementary particles known as atoms.
- ✓ Chemists have identified around a hundred elements that make up the composition of all material substances.

2. States and Macroscopic Characteristics of Matter

- ✓ *Matter*: Matter is anything that has mass and occupies space.
- ✓ *States of Matter*: Matter can exist in three different physical states:
- ✓ *Solid state*: It has a defined volume and shape.
- ✓ *Liquid state*: It has a defined volume but no specific shape; it takes the shape of its container.
- ✓ *Gaseous state*: It has neither a defined volume nor a defined shape; it takes both the volume and shape of its container.

Heat and cold play essential roles in the transition of a substance from one state to another depending on the temperature (T) and pressure (P):



States of Matter

Property	Solids	Liquids	Gases
Shape	Definite shape	No definite shape, takes shape of the container	No definite shape, takes shape of the container
Volume	Definite volume	Definite volume	No fixed volume
Particle Arrangement	Tightly packed Solid	Close together but can move Liquid	Far apart, can move Gas
Particle Motion	Vibrating in a fixed position	Flowing and sliding past each other	Moving rapidly and freely
Example	Ice, Wood, Stone	Water, Oil, Milk	Air, Oxygen, Nitrogen

Figure I.1: States of Matter.

3. Changes in the State of Matter

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

Examples:

-Melting point of water: 0°C;

-Melting point of copper: 1084°C.

3.1. Physical Changes

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.

Matter can transition from one state to another under specific temperature and pressure conditions.

The transition of matter from a solid state to a liquid state is achieved through melting, from a liquid state to a gaseous state through vaporization, and from a solid state to a gaseous state through sublimation.

These transformations are illustrated in the diagram below:

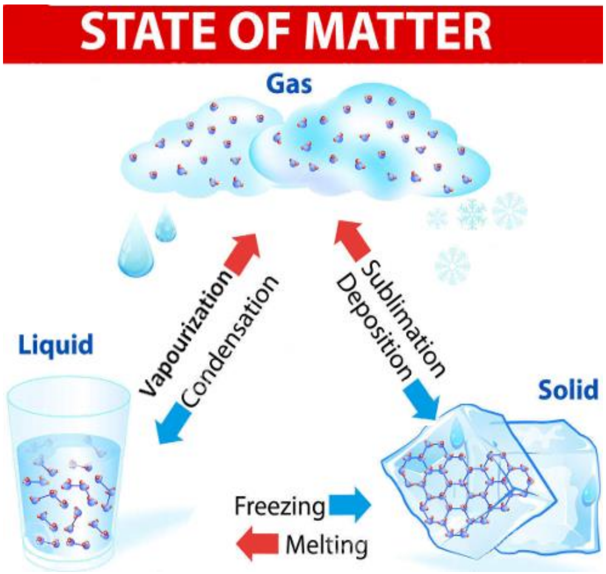


Figure I.2: Changes in the State of Matter.

3.2. Chemical Changes

A chemical change is a transformation that alters the nature of a substance through a chemical reaction.

Examples:

- Corrosion: Iron rusts.
- Combustion: Wood burns to produce ash and gases.

- Chemical changes can be identified by certain indicators, such as:
- Formation of a gas;
- Formation of a precipitate;
- Change in color;
- Release of energy in the form of light and heat.

4. Notions of Atom, Molecule, Mole, and Avogadro's Number

4.1. Atom

An atom is the smallest unit of an element that can exist.

Atoms combine to form molecules.

An atom consists of a nucleus around which electrons are in motion.

The nucleus has an incredibly small diameter of approximately $10\approx^{-14}$ meters.

It is composed of nucleons (protons and neutrons) and contains almost all of the atom's mass.

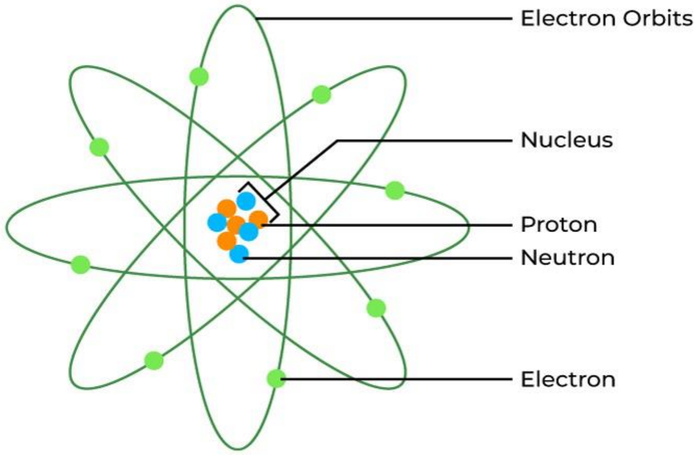


Figure I.3: Atom structure.

4.2. Molecule

A molecule is the association of two or more atoms (e.g., NaCl, H_2O, O_2) bonded together by chemical bonds. It is the smallest part of a compound that retains its properties. A molecule is characterized by its molecular formula and its molecular molar mass.

Examples:

- H_2O (water);
- H_2 (hydrogen gas);
- HCl (hydrochloric acid);
- H_2SO_4 (sulfuric acid);

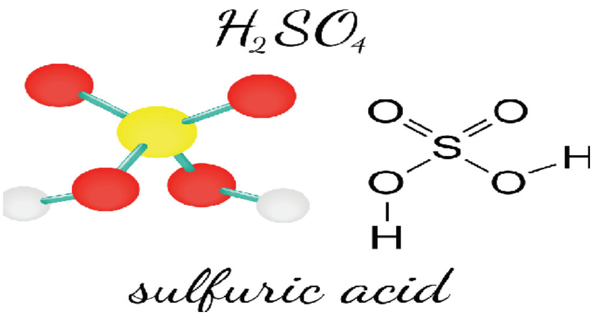


Figure I.4: H_2SO_4 Molecule.

4.3. Mole and Avogadro's Number

The mole is a unit of measurement for the amount of substance in a system containing N identical entities. It is defined as the ratio between the mass of the sample (m), expressed in grams (g), and the molar mass (M), expressed in grams per mole (g/mol).

$$\mathbf{n = m / M}$$

Where:

- ✓ N is the number of moles.
- ✓ m is the mass of the compound in grams (g).
- ✓ M is the molar mass of the compound in grams per mole (g/mol).

For example, to find the number of moles in 36 g of water:

$n = m_{water} / M_{water} = 36$ g / 18 g/mol = 2 moles.

The number of atoms contained in a mole is called Avogadro's Number (NA), $NA = 6.023\times10^{23}$.

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

The quantity of matter, denoted as "n," is proportional to the number of molecules, denoted as "N," contained within a substance.

$N = n\ x\boldsymbol{NA}$ where $n = N/\boldsymbol{NA}$.

Example:

A sample of copper oxide, CuO, has a mass m = 1.59 g. How many moles and molecules of CuO, as well as atoms of Cu and O, are in this sample? MCu = 63.54 g/mol; MO = 16 g/mol.

Solution:

Number of moles of CuO: n = m / MCuO = 1.59 / (63.54 + 16) = 0.01999 moles.

Number of molecules of CuO = (m / MCuO) x NA = 0.12×10^{23} molecules.

Number of Cu atoms = Number of O atoms = (m / MCuO) x NA = 0.12×10^{23} atoms.

5. Concepts of Atomic Mass Unit, Atomic and Molecular Molar Mass, and Molar Volume

5.1. Atomic Mass Unit (AMU)

The masses of particles such as electrons, protons, neutrons, etc., are not convenient to express in kilograms (Kg) due to their very small scale. Instead, a different unit of mass called the Atomic Mass Unit (AMU) or "u" is used. One atomic mass unit is defined as one-twelfth the mass of a 12 C.

In other words, 1 u (AMU) is defined as 1/12th of the mass of one 12 C atom.

So: *1amu= (1/12). 12/NA (g) = 1/ NA (g) =*$1.66.10^{-24}$ *(g)* **= 1,66.** $\mathbf{10^{-27}}$ **Kg.**

Example:

Determine the mass of one sodium (Na) atom, knowing that its atomic molar mass is 23 g/mol.

Solution:

1 mol $\longrightarrow$ 23 g $\longrightarrow$ 6.023 10^{23} atom

1 atom Na $\longrightarrow$ m_{Na} g $\longrightarrow$ 1 tome

$m = \frac{23}{6.023\ 10^{23}} = 3.8\ 10^{-23}$ g

5.2. Atomic Molar Mass

Atomic molar mass is the mass of one mole of atoms. Atomic molar mass = NA x mass of a single atom (g/mol).

Examples:

Molar mass of hydrogen (H): M(H)= $1{,}674.10^{-24}$g x *N*A= 1,0079 g.mol^{-1};

Molar mass of oxygen (O): M(O)= $2{,}657.10^{-23}$g x *N*A= 16 g. mol^{-1}.

5.3. Molecular Molar Mass

The molecular molar mass of a molecular compound is the mass of one mole of molecules. It is equal to the sum of the molar masses of its constituent elements.

Examples:

Molar mass of CO_2: M(CO_2)= M(C) + 2.M(O)= 44 g/mol ;

Molar mass of H_2O: M(H_2O)= M(O) + 2.M(H)= 18,02 g/mol.

5.4. Molar Volume

Under normal conditions of temperature and pressure (NTP: 0°C and 101325 Pa (1 atm)), one mole of gas molecules always occupies the same volume. This volume is the molar volume (MV):**MV = 22.4 L/mol.**

Under these conditions, the number of moles can be calculated as follows: n = V/MV = V/22.4.

Example:

Number of moles in 11.2 liters of carbon dioxide gas: $n = V_{gas}/V_{molar} = 11.2/22.4 = 0.5$ moles.

6. Law of Conservation of Mass (Lavoisier) in Chemical Reactions

The law of conservation of mass, as stated by Lavoisier, is: "In a chemical reaction, the total mass of the reactants is equal to the total mass of the products formed," which means that nothing is lost, nothing is created; everything is transformed.

This law is considered the foundation of the quantitative study of all chemical reactions.

Through a chemical reaction, the elements are conserved, and the mass of the reactants consumed is equal to the mass of the products formed.

For the reaction to accurately represent the phenomenon, it must always be balanced.

For example:

Consider one sulfur atom and two oxygen atoms arranged in a certain way to always yield one sulfur atom and two oxygen atoms, but

arranged differently: $S + O_2 \rightarrow SO_2$

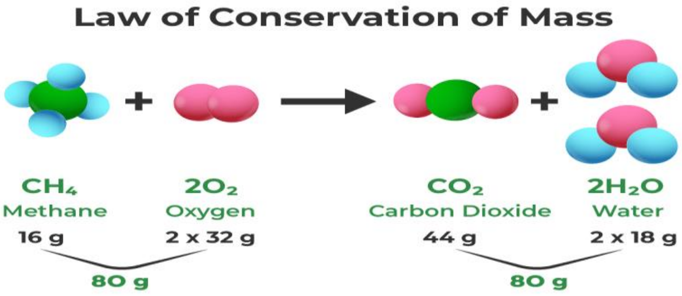


Figure I.5: Law of conservation of mass.

7. Qualitative Aspect of Matter

7.1. Pure Substances, Homogeneous and Heterogeneous Mixtures

A pure substance is a substance composed of only one type of chemical entity (atom, ion, or molecule).

A pure substance can be either an element (simple pure substance, e.g., Cu, Fe, H_2, O_2...) or a compound (composed of multiple elements, e.g., pure water H_2O).

A mixture is a substance composed of several types of chemical entities mixed together. Mixtures can be either homogeneous (such as saltwater...) or heterogeneous (having two or more distinct phases, for example, water and oil...).

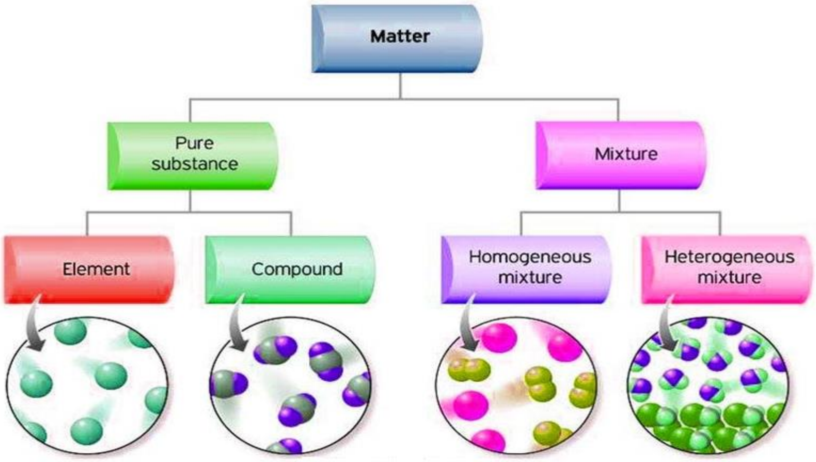


Figure I.6: Classification of Matter.

7.2. Solutions, Solute, Solvent, Aqueous Solution, Dilution, and Saturation Solutions

A **solution** is a homogeneous mixture of two or more components, which can be in a liquid, gaseous, or solid phase.

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

The **solute** is a chemical species (molecular or ionic) that is dissolved in a solvent. The solvent is always present in a much larger quantity than the solute.

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

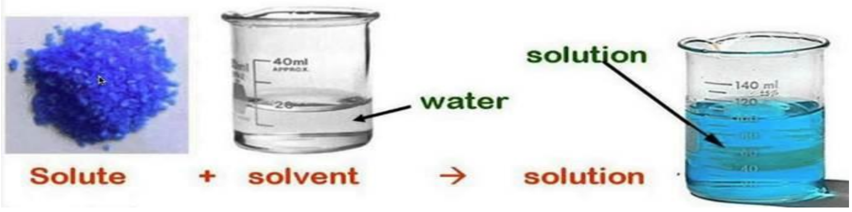


Figure I.7: Solute, Solvent and Solution.

Dilution is a process that involves obtaining a final solution with a lower concentration than the initial one, either by adding a solvent or by taking a portion of the solution and then adding solvent to maintain the same volume. Dilution is characterized by its dilution factor.

This concept assumes that the substance being diluted is soluble in the chosen solvent.

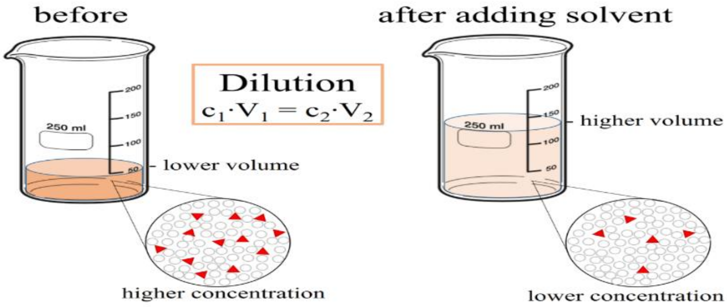


Figure I.8: Dilution.

A saturated solution is obtained by dissolving a solute in a solvent; the solution is saturated when the introduced solute can no longer dissolve and forms a precipitate.

Figure I.9: Solutions: Unsaturated, Saturated, and Supersaturated.

8. Quantitative Aspect of Matter

In physical chemistry, certain quantities have a quantitative aspect of matter, such as density, different types of concentrations, and mass density.

8.1 Concentrations:

Concentrations are quantities with units used to determine the proportion of solutes to that of the solvent. Depending on the chosen unit, we distinguish:

a. Molarity (Molar Concentration) (MC) It expresses the number of moles of solute per liter of solution.

$$C_n = n/V$$

b. Mass Concentration: Mass concentration, also known as content, is the mass in grams of the solute per liter of solution. Its symbol is Cm, and its unit is grams per liter ($g \cdot L^{-1}$). It can be referred to as the partial mass density of a component of the solution:

$$C_m = m/V$$

There is a relationship between molar concentration and mass concentration:

$$C_m = C_n \times M.$$

8.2 Molality

Molality expresses the amount of solute contained in 1 kg of solvent:

molality = moles of solute / mass of solvent (kg)

8.3 Normality (N)

Normality expresses the number of gram equivalent weights of solute per liter of solution (geq/L). The gram equivalent weight is the quantity of substance that contains one mole of the species in question (H^+, OH^-, e^-..).

$$N = g\text{eq} / V$$

Relationship between N: Normality and Cn: Molarity: N = Cn x valence (Z).

Meaning of Z, Examples:

a. In the case of an acid: Z is the number of $H+$ protons involved.
   HCl (Z=1); H_2SO_4 (Z=2); H_3PO_4 (Z=3);
b. In the case of a base: Z is the number of OH^- ions involved, e.g.:
   $NaOH$ (Z=1); $Ca(OH)_2$ (Z=2);
c. In the case of salts: Z is the number of metal cations multiplied by the valence of that metal. Na_2SO_4 (Z=2 × (+1) = 2) ($2Na^+$; SO_4^{2-}); Meq (Na_2SO_4) = M(Na_2SO_4)/2;
d. In the case of redox reactions: Z is the number of electrons transferred, e.g.:
   $KMnO_4$: Z=5 $MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightleftarrows Mn^{2+}(aq) + 4\,H_2O(l)$.

8.4 Percentage (%)

The mass percentage % of a solution indicates the mass of a substance per 100g of the solution. It is a weight-to-weight comparison.

The volume percentage % of a solution indicates the volume of a substance per 100 L of the solution. It is a volume-to-volume comparison.

Example:

Calculate the theoretical weight/weight percentages of C, H, and O in the ethanol molecule C_2H_5OH.

Data: $A.M_C$= 12.0111 amu; $A.M_H$= 1.008 amu; $A.M_O$= 15.999 amu.

Solution:

For one mole of ethanol, there are:

2 atomic grams of C × 12.011 g/atomic gram = 24.022 g of C;

6 atomic grams of H × 1.008 g/atomic gram = 6.048 g of H;

1 atomic gram of O × 15.999 g/atomic gram = 15.999 g of O;

Hence, the molar mass of ethanol = $2AM_C + 6AM_H + AM_O$ = 46.069 g.

For 100 g of ethanol, there are:

24.022 g/46.069 g × 100 = 52.14 % of C;

6.048 g/46.069 g × 100 = 13.13 % of H;

15.999 g/46.069 g × 100 = 34.73 % of O.

8.5 Mass density

Density expresses the mass of a certain volume of a solution under specific temperature and pressure conditions. It is denoted as ρ, and its unit is g/L: Mass density $\rho = m/v$.

Example: Determine the density of ether, knowing that half a liter of ether weighs 358 g.

Solution: Mass density $\rho = m/v = 358$ g/0,5 L = 716 g/L.

8.6 Density

8.6.1. Density of Solids and Liquids Relative to Water

Relative density (d) is the ratio of the density of a substance to the density of a reference substance. For solids and liquids, the reference substance is pure water, which has a density of 1 kg/liter.

The density of a liquid or solid is the ratio of the density of that liquid or solid to the density of water. In mathematical terms, it is expressed as:

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

Example 1:

Calculate the density of iron, given that the densities of iron and water are 7.8 g/cm^3 and 1 g/cm^3, respectively (1 cm^3 = 10^{-3} L, and 1 mL = 1 cm^3).

Solution: $d = \rho/\rho$water =7,8/1= 7.8.

Example 2:

You have a commercial bottle of HCl solution (purity = 36%, density = 1.18 g/mL, Molar Mass= 36.46 g/mol). What is the molar concentration of the commercial HCl solution?

Solution:

d = 1.18 1 liter of solution = 1000 mL (weighs) $\Longrightarrow$ 1180g of solution $\Longrightarrow$ mg of pure HCl;
36% means: 100g of solution $\Longrightarrow$ 36g of pure HCl; So, m = 1180g * (36/100) $\Longrightarrow$ m = 424.8 g ;
M = m/n $\Longrightarrow$ n = m/M $\Longrightarrow$ n = 424.8 / 36.46 $\Longrightarrow$ n = 11.65 mol ;
11.65 moles is the amount of pure HCl calculated from the mass found in 1180g of solution, and this is equivalent to one liter of solution $\Longrightarrow$ C = 11.65 mol/L.

8.6.2. Density of Gases Relative to Air

The density of a gas relative to air is equal to the ratio of the mass (m) of a volume (v) of the gas to the mass m_{air} of the same volume of air (reference substance), with both masses measured under the same conditions of temperature and pressure.

This relationship is expressed as d = mass of the gas / mass of air = $\rho \times V / \rho_{air} \times V$, which simplifies to $d = \rho / \rho_{air}$.

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

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

Thus: d = mass of the gas / mass of air = $\boldsymbol{d} = M/29$. Density has no unit.

Example: Calculate the molar mass of air under standard conditions (P=1atm; T=25°C; n= 1mol).

Solution:

Under standard conditions, the density of air is 1.293 g/L.

We know: 1 mol of air $\longrightarrow$ 22,4 L

So, the mass of air corresponding to 22.4 L is equal to the molar mass of air:

1 mol of air $\longrightarrow$ 22,4 L $\longrightarrow$ M (air)

1 L of air $\longrightarrow$ 1,293 g

22,4 L of air $\longrightarrow$ M (air) ; M (air) = 1,293 x 22,4 = 29

8.7 Mole Fraction (Xi)

The mole fraction (Xi) indicates the ratio of the number of moles of a specific component to the total number of moles in the solution. In a solution, you have:

Σ Xi = 1 (The sum of the mole fractions of all components of the solution is always equal to 1).

Observations:

- A solution is considered molar for a given solute when its concentration (MC) is 1 mol/L.
- It is considered decimolar when MC is 10^{-1} mol/L.
- It is considered millimolar when MC is 10^{-3} mol/L.
- When substances are present in trace amounts in a solution, it is common to use the terms Parts Per Million (ppm) = 1 mg/L, Parts Per Billion (ppb) = 0,001 mg/L, and Parts Per Trillion (ppt) = 0,000001 mg/L.

Example:

We completely dissolve 1g of NaCl in 90 mL of water with a density of 0.998 g/mL. We obtain an aqueous solution of Sodium Chloride of 90 mL.

1-What is the mass percentage of NaCl in this solution.

2-What is the mole fraction of NaCl in this solution.

3-What is the molality of NaCl.

4- What is the molar concentration of NaCl. M(Na): 23g/mol; M(Cl): 35.5g/mol.

Solution:

What is the mass percentage of NaCl in this solution?

% NaCl = $m_{NaCl} / (m_{NaCl} + m_{H2O})$ x 100

$m_{H2O} = \rho_{H2O}$ x V_{H2O} = 0.998 x 90 = 89.82 g

$\% NaCl = 1 / (1 + 89.82) \times 100 = 1.1\%$

2- What is the mole fraction of NaCl in this solution?

$\% NaCl (molar) = n_{NaCl} / (n_{NaCl} + n_{H2O}) \times 100$

$n_{NaCl} = m_{NaCl} / M_{NaCl} = 1 / (23 + 35.5) = 0.017$ mol

$n_{H2O} = m_{H2O} / M_{H2O} = 89.82 / 18 = 4.99$ mol

$\% NaCl (molar) = 0.017 / (0.017 + 4.99) \times 100 = 0.34\%$

3- What is the molality of NaCl.

Molality = n_{NaCl} / m_{H2O}

Molality = $0.017 / (89.82 \times 10^{-3}) = 0.19$ mol/kg.

4- What is the molar concentration of NaCl?

CM (molar concentration) = n_{NaCl} / V_{H2O}

CM = $0.017 / (90 \times 10^{-3}) = 0.188$ mol/l

8.8 Degree

Degree concentration, denoted as D or (°), is defined as the mass of pure solute in 100g of solution. It is often found on the labels of products like bleach or vinegar.

Example: Vinegar Acidity Degree

Vinegar is a solution of acetic acid in water. Its acidity degree represents the mass percentage of acid in the solution. If you read on the label of the vinegar: "vinegar 5°" or "5D", what is its molarity?

Solution:

The acidity degree (D or °) of vinegar is defined as the mass of pure acetic acid (5g) contained in 100g of vinegar.

Since the density of vinegar is similar to that of water, a liter of 5° vinegar contains approximately 50g of acetic acid, which represents a concentration of about 0.83 mol/L (M_{CH_3COOH}=60 g/mol).

Corrected Exercises

Exercise 01:

Calculate the number of sulfur S, hydrogen H and oxygen O atoms obtained in 49g of sulfuric acid (H_2SO4).

Exercise 02:

A copper oxide CuO sample has a mass of m = 1.59g. How many moles and molecules of CuO and atoms of Cu and O are there in this sample?

Exercise 03:

We are given the following atomic masses in amu: N = 14, O = 16, $La(NO_3)_3$ = 324.9.

1. What is the atomic mass of Lanthanum (La) in amu?
2. Given that the molar mass of Lanthanum is M=138.9 g/mol, what is the mass in grams of Lanthanum in a mixture of 0.1 mol of $La(NO_3)_3$ and 1 mol of La_2O_3?
3. Calculate the number of Lanthanum atoms in this mixture.

Exercise 04:

Questions A, B, C, D, E are independent.

A. What volume of the following solution is needed to obtain 0.1 g of dissolved substance: $Ca(OH)_2$ at 10^{-2} M?

B. Calculate the concentration in mol/L of 150 mL of an NH_3 solution at 2 mol/L diluted to 500 mL.

C. What respective volumes of 1.5 M and 0.8 M aqueous hydrochloric acid solutions must be mixed to obtain 600 mL of a 1.2 M solution?

D. What is the mass of pure sulfuric acid contained in 200 cm^3 of a 0.4 N H_2SO_4 solution?

E. What volume of water must be added to 200 mL of an HCl solution (0.5 M) to obtain a solution with a concentration of 0.08 M?

Exercise 05:

Dissolve a 5g sugar lump (sucrose) in a 50 mL cup. Calculate its mass concentration and molarity. $M(C_{12}H_{22}O_{11})$ =342 g/mol.

Exercise 06

The solubility of aluminum sulfate is 100 g in 900 g of water. The density of the saturated solution at 15°C is 1.106, M ($Al_2(SO_4)_3$) = 342 g/mole. Calculate:

A. The molarity;

B. The molality;

C. The mole fraction;

D. The % weight/weight;
E. The % weight/volume.

Exercise 07:

Calculate the molarity of one liter of a phosphoric acid solution with a density of 1.08 and 65% by weight of H_3PO_4. What is its normality?

Exercise 08:

An aqueous solution with 4% HCl concentration is prepared, the density of this solution being 1.02 g/cm^3, what is the molality of this solution?

Exercise 09:

Calculate the concentration C of chloride ions (in mol/L and g/L) in a solution obtained by mixing two solutions: 90 cm^3 of NaCl 0.75 M and 75 cm^3 of $CaCl_2$ 0.6 M.

Exercise 10:

2 kg of phosphoric acid solution contains 200 g of pure phosphoric acid. What is the molarity of the solution ($d_{solution}$ =1,053).

Correction

Exercise 1:

Molar mass of H_2SO_4=(2×1)+(1×32)+(4×16)=2+32+64=98 g/mol.

The number of moles of a substance is given by: $n=\frac{m}{M}=\frac{49}{98}=0.5$ mol.

Sulfur atoms (S): Since 1 mole of H_2SO_4 contains 1 mole of sulfur atoms, the number of moles of sulfur atoms is the same as the moles of H_2SO_4 =0.5 mol

To find the number of atoms, multiply by Avogadro's number (6.023×10^{23})

Number of sulfur atoms=$0.5\times6.023\times10^{23}$=$\mathbf{3.011\times10^{23}}$ **atoms.**

Hydrogen atoms (H): Since 1 mole of H_2SO_4 contains 2 moles of hydrogen atoms, the number of moles of hydrogen atoms is 2×0.5=1 mol

Thus, the number of hydrogen atoms is: $1\times6.023\times10^{23}$=$\mathbf{6.023\times10^{23}}$ **atoms**

Oxygen atoms (O): Since 1 mole of H_2SO_4 contains 4 moles of oxygen atoms, the number of moles of oxygen atoms is 4×0.5=2 mols.

Thus, the number of oxygen atoms is: $2\times6.023\times10^{23}$=$\mathbf{1.204\times10^{24}}$ **atoms**

Exercise 2:

Number of moles of CuO: $n=\frac{m}{M_{CuO}}=\frac{1.59}{63.54+16}=0.01999$ moles.

Number of molecules of CuO $=\frac{m}{M_{CuO}}N_A=0.12\times10^{23}$ molecules.

Number of Cu atoms = number of O atoms = $\frac{m}{M_{CuO}} N_A$ = 0.12×10^{23} atoms

Exercise 3:

1. The atomic mass of Lanthanum (La) in amu

Mass of nitrogen in $La(NO_3)_3 = 3 \times 14 = 42$ amu.
Mass of oxygen in $La(NO_3)_3 = 9 \times 16 = 144$ amu.
So, the total mass contribution from nitrogen and oxygen is: 42+144=186 amu.
Now, subtract this from the total molar mass of $La(NO_3)_3$ to find the atomic mass of Lanthanum: Atomic mass of La=324.9g/mol−186g/mol=138.9g/mol.
The atomic mass of Lanthanum (La) is **138.9 amu**.

2. The mass in grams of Lanthanum in a mixture of 0.1 mol of $La(NO_3)_3$ and 1 mol of La_2O_3

The molar mass of Lanthanum is 138.9 g/mol.
For **$La(NO_3)_3$**, the number of Lanthanum atoms is 1 per formula unit, so 0.1 mol of $La(NO_3)_3$ contains 0.1 mol of Lanthanum.
For **La_2O_3**, there are 2 Lanthanum atoms per formula unit, so 1 mol of La_2O_3 contains 2 mol of Lanthanum.
The total number of moles of Lanthanum in the mixture is: 0.1 mol+2 mol=2.1 mols.
Now, to find the mass of Lanthanum in this mixture:
Mass of La=moles of La×molar mass of La
Mass of La=2.1mol×138.9g/mol=291.69g
Thus, the mass of Lanthanum in the mixture is **291.69 grams**.

3. Calculate the number of Lanthanum atoms in this mixture.

Number of Lanthanum atoms=moles of La×N_A
Number of Lanthanum atoms=2.1mol×6.023×10^{23}atoms/mol =1.2646×10^{24} atoms
Thus, the number of Lanthanum atoms in the mixture is approximately **1.26×10^{24}** atoms.

Exercise 4:

A. Molar mass of $Ca(OH)_2$=74.096g/mol.

moles of $Ca(OH)_2$= $\frac{\text{mass}}{\text{molar mass}} = \frac{0.1\text{g}}{74.096\text{g/mol}} \approx 0.00135\text{mol}$

Molarity (M)= $\frac{\text{moles of solute}}{\text{volume of solution (L)}}$

Volume of solution (L) = $\frac{\text{moles of solute}}{\text{Molarity (M)}} = \frac{0.00135\text{mol}}{0.01}$ = 0.135 L= 135 mL

To obtain 0.1 g of $Ca(OH)_2$ dissolved in a 0.01 M solution, you need **135 mL** of the solution.

B. To calculate the new concentration after dilution, we can use the dilution formula**:** $\mathbf{C_1V_1=C_2V_2}$

$(2mol/L) \times (0.150L) = C_2 \times (0.500L)$

0.3 mol=C2×0.500 L.

$C_2=\frac{0.3mol}{0.500L}=0.6mol/L$.

The concentration of the NH_3 solution after dilution is **0.6 mol/L**.

C. The formula for mixing two solutions is:$C_1V_1+C_2V_2=C_{final}V_{final}$

$$\begin{cases} 1.5.\ V_1 + 0.8\ V_2 = 1.2\times0.600\ (V_{final}= 600\ mL=0.600L) \\ V_1+V_2 = 600\ mL = 0.600\ L \end{cases}$$

V_1=0.3429 L=342.9 mL

V_2= 0.600−0.3429= 0.2571 L= 257.1 mL

To obtain 600 mL of a 1.2 M hydrochloric acid solution:

- You need **342.9 mL** of 1.5 M HCl,
- You need **257.1 mL** of 0.8 M HCl.

D. N= x×M.

$M=\frac{N}{X}=\frac{0.4}{2}= 0.2$ mol/L

$C=\frac{n}{V} \longrightarrow n= C.V = \frac{m}{M}$

$m= C.\ V\ .M = 0.2\ .\ 200.10^{-3}.\ 98 = 3.92$ g.

The mass of pure sulfuric acid in 200 cm^3 of a 0.4 N H_2SO_4 solution is **3.92 g**.

E. We know that the dilution equation is: $\mathbf{C_1V_1=C_2V_2}$

$0.5M\times0.200L=0.08M\times V_2$

$V_2=\frac{0.1}{0.08}=1.25L$

The final volume is 1.25 L, and the initial volume is 0.200 L. The volume of water to be added is: $V_2-V_1=1.25L-0.200L=1.05L$.

You need to add 1.05 L of water to 200 mL of the 0.5 M HCl solution to obtain a final concentration of 0.08 M.

Exercise 5:

Mass concentration is the amount of solute (in grams) per unit volume of solution (in liters). The formula for mass concentration is:

$$\text{Mass Concentration}=\frac{\text{Mass of solute}}{\text{Volume of solution in L}}=\frac{5}{0.05}= 100\ g/L.$$

$$n=\frac{m}{M}=\frac{\text{Mass of sucrose}}{\text{Molar mass of sucrose}}=\frac{5g}{342g/mol}= 0.01462\ mol.$$

Molarity$= \frac{\text{Moles of sucrose}}{\text{Volume of solution in L}} = \frac{0.01462\text{mol}}{0.050\text{L}} = 0.2924\text{mol/L}$

Exercise 6:

A. Molarity

$n = \frac{m}{M} = \frac{\text{Mass of } Al_2(SO_4)_3}{\text{Molar mass of } Al_2(SO_4)_3} = \frac{100\text{g}}{342\text{g/mol}} = 0.2924$ mol.

Mass of solution= mass of aluminum sulfate + mass of water= 100g+900g=1000g

Volume of solution $= \frac{\text{Mass of solution}}{\text{Density}} = \frac{1000\text{g}}{1.106\text{g/mL}} = 903.3\text{mL} = 0.9033\text{L}$

Molarity$= \frac{\text{Moles of } Al_2(SO_4)_3}{\text{Volume of solution in L}} = \frac{0.2924\text{mol}}{0.9033\text{L}} = 0.323\text{mol/L}$.

So, the molarity is **0.323 mol/L**.

B. Molality

Molality (m) is the number of moles of solute per kilogram of solvent (water). The mass of the solvent (water) is 900 g = 0.900 kg. Using the moles of $Al_2(SO_4)_3$ calculated earlier:

Molality$= \frac{\text{Moles of } Al_2(SO_4)_3}{\text{Mass of water in kg}} = \frac{0.2924 \text{ mol}}{0.900 \text{ kg}} = 0.325$ mol/kg

So, the molality is **0.325 mol/kg**.

C. Mole Fraction

The mole fraction of a component is the number of moles of that component divided by the total number of moles in the solution.

First, calculate the moles of water:

Moles of water$= \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{900 \text{ g}}{18 \text{ g/mol}} =50$ mol

Now, the total moles in the solution is the sum of the moles of aluminum sulfate and the moles of water:

Total moles=Moles of $Al_2(SO_4)_3$+Moles of water=0.2924 + 50 =50.2924 mol.

Mole fraction of $Al_2(SO_4)_3 = \frac{\text{Moles of } Al_2(SO_4)_3}{\text{Total moles}} = \frac{0.2924\text{mol}}{50.2924\text{mol}} = 0.0058$.

Mole fraction of water = 1 – 0058 = 0.9932

D. % Weight/Weight

The weight/weight percentage (% w/w) is the mass of the solute (aluminum sulfate) divided by the total mass of the solution, multiplied by 100:

% w/w$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100 = \frac{100 \text{ g}}{1000 \text{ g}} \times 100 = 10$

So, the weight/weight percentage is **10%**.

E. % Weight/Volume

The weight/volume percentage (%w/v) is the mass of the solute (aluminum sulfate) divided by the volume of the solution in mL, multiplied by 100:

% w/v= $\frac{\text{Mass of solute}}{\text{Volume of solution in mL}}$x100= $\frac{100\text{ g}}{903.3\text{ mL}}$×100 = 11.08%

So, the weight/volume percentage is approximately **11.08%**.

Exercise 7:

The mass of 1 liter of solution can be calculated using its density:

Mass of solution=Density × Volume=1.08 g/mL×1000 mL=**1080 g.**

Since the solution is 65% by weight H_3PO_4, the mass of H_3PO_4 in 1 L of solution is:

Mass of H_3PO_4=65%×1080 g=0.65×1080 g=**702 g.**

n of H_3PO_4= $\frac{\text{Mass of } H_3PO_4}{\text{Molar mass of } H_3PO_4} = \frac{702\text{g}}{98\text{g/mol}}$ =7.16 mol.

Molarity= $\frac{\text{Moles of } H_3PO_4}{\text{Volume of solution in L}} = \frac{7.16\text{mol}}{1\text{L}}$ =7.16 M.

Normality= x. Molarity = 3. 7.16= 21.48 N.

Exercise 8:

The volume of the solution is given as 1 L. Using the density, we can find the mass of the solution:

Mass of solution= Density × Volume = 1020 g/L×1 L=1020 g.

The solution has 4% HCl by weight, so the mass of HCl in the 1020 g of solution is:

Mass of HCl=4%×1020 g=0.04×1020 g=40.8 g.

n of HCl= $\frac{\text{Mass of HCl}}{\text{Molar mass of HCl}} = \frac{40.8\text{g}}{36.46\text{g/mol}}$ =1.12mol.

Since the solution consists of HCl and water, the mass of the solvent (water) is:

Mass of water=Mass of solution−Mass of HCl=1020 g−40.8 g = 979.2 g = 0.9792 kg.

Molality= $\frac{\text{n of HCl}}{\text{Mass of water in kg}} = \frac{1.12\text{mol}}{0.9792\text{kg}}$ = 1.14mol/kg = 1.14 m

The molality of the solution is **1.14 mol/kg**.

Exercise 9

n NaCl= C_{NaCl}×V=0.75×0.090=0.0675mol.

Since 1 mole of NaCl produces 1 mole of Cl^-, the moles of Cl^- ions from NaCl are:

$n_{Cl-\text{ (from NaCl)}}$=0.0675mol.

n_{CaCl2}= C_{CaCl2} × V= 0.6×0.075=0.045mol.

Since 1 mole of $CaCl_2$ produces 2 moles of Cl^-, the moles of Cl^- ions from $CaCl_2$ are:

$n_{Cl-\text{ (from CaCl2)}}$= 2×0.045 = 0.090mol.

$n_{Cl-\text{ (total)}} = n_{Cl-\text{ (from NaCl)}} + n_{Cl-\text{ (from CaCl2)}}$ = 0.0675 + 0.090 = 0.1575mol.

V_{total}=90 cm^3 + 75cm^3 =165 cm^3= 0.165L.

C_{Cl-}= $\frac{n_{Cl-\text{(total)}}}{V_{total}} = \frac{0.1575}{0.165}$ = 0.9545 M.

$C_{Cl^-}(g/L) = C_{Cl^-} \times M_{Cl^-} = 0.9545 \times 35.45 = 33.84g\ /L.$

Exercise 10

Using the density formula: Density= $\frac{\text{Mass}}{\text{Volume}}$

Vsolution= $\frac{m_{\text{solution}}}{d_{\text{solution}}} = \frac{2000\text{ g}}{1.053}$ =1899.24 mL=1.899 L.

n (H_3PO_4) = $\frac{m_{\text{H3PO4}}}{M_{\text{H3PO4}}}$ m = $\frac{200\text{g}}{98.00\text{g/mol}}$ = 2.041mol.

C (H_3PO_4) = $\frac{n_{\text{H3PO4}}}{V_{\text{solution}}} = \frac{2.041\text{mol}}{1.899\text{L}}$ =1.075M.

The molarity of the phosphoric acid solution is: **1.075 M.**

Chapter II:
Main Constituents of Matter

1. Introduction

To identify the various elementary particles of matter, several experiments were conducted. These particles were discovered between 1875 and 1910, and they include the proton, neutron, and electron.

Electron: The characteristics of the electron were obtained from the following experiments:

a. Crookes' Experiment (1879) and characteristics of cathode rays.
b. J.J. Thomson's Experiment (1895): Determination of the ratio |e|/m (charge-to-mass ratio) of the electron.
c. Robert Millikan's Experiment (1908): Determination of the charge |e| of the electron and deduction of its mass.

Proton: Goldstein's experiment: Demonstration of the positive charge of the nucleus.

Neutron: Chadwick's experiment: Demonstration of the existence of the neutron within the nucleus.

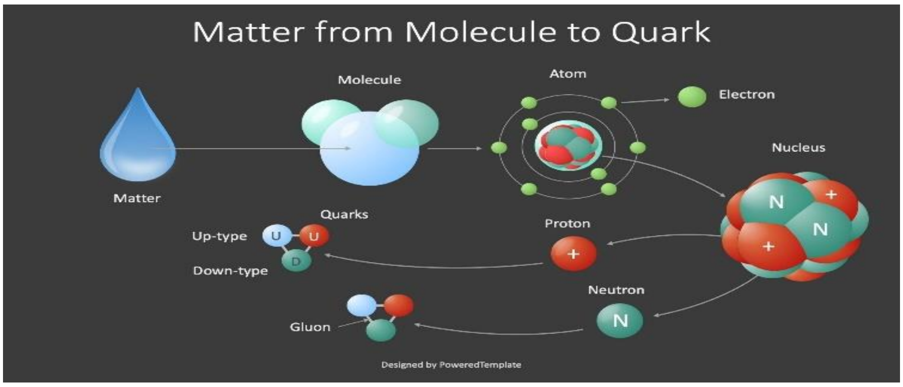


Figure II.1: The Various Constituents of Matter.

2. Faraday's Experiment

Faraday's experiments suggest the existence of a relationship between matter and electricity. To confirm this proposition, a large number of measurements were carried out using a voltameter, establishing a connection between the masses of products released during electrolysis and the corresponding quantities of electricity.

Based on these measurements, Faraday formulated two laws:

a. The mass of an element that appears at the electrode (liberated during a given time) is proportional to the amount of electricity that passes through the electrolysis during that time.
b. Electrochemical equivalents coincide with chemical equivalents, meaning that regardless of the electrolyte used (monovalent, divalent, trivalent, etc.), the quantity of electricity required to liberate one chemical equivalent of a substance remains the same.

For **example**, the amount of electricity required to decompose one mole of NaCl is equal to $N_A = 6{,}023\ 10^{23}$. $1{,}6\ 10^{-19} = 96486$ coulombs, and this quantity is called the Faraday. Therefore, 1 Faraday (1 F) is approximately equal to 96,500 coulombs, and this quantity can transform any ion.

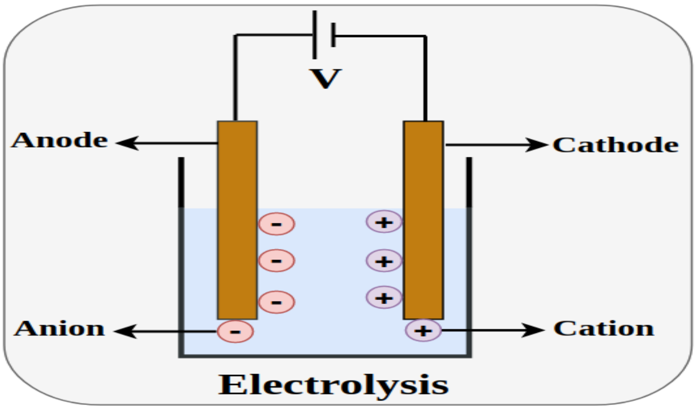


Figure II.2: Movement of Ions During Electrolysis

3. Identification of the Constituents of Matter

From these three elementary particles (electron, proton, and neutron), each with very small dimensions, all the matter in the universe can be composed. These three building blocks were discovered between 1875 and 1910.

3.1 Electron

3.1.1. Crookes' Experiment (1869-1875)

Comprehensive studies of matter were conducted by William Crookes during the latter half of the 19th century. These studies were carried out using a discharge tube represented in the figure below:

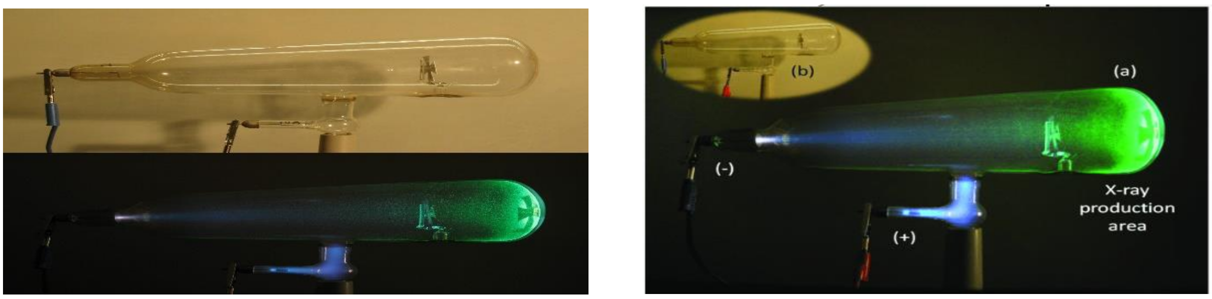


Figure II.3: Schematic View of a Crookes Tube

This experiment involved reducing the gas pressure (air, neon, helium, etc.) in the glass tube to approximately 10^{-6} atm. The glass bulb has two metallic pieces at its ends referred to as "electrodes": an aluminum cathode and an anode, which serves as the target for electrons.

A voltage of approximately 15,000 volts is applied between the two electrodes.

He then noticed the appearance of a bluish light forming on the surface of the glass. This radiation originates from the electrode connected to the (-) terminal of the voltage generator, called the cathode.

In 1876, E. Goldstein gave a name to this radiation, calling it "cathode rays". This radiation is visible if the bulb contains a gas at low pressure.

Cathode rays travel in straight lines and are deflected when approaching a magnet or a charged object: they are attracted to positively charged objects and repelled if the object is negatively charged.

3.1.2. J.J. Thomson's Experiment (1895): Determination of the |e|/m Ratio

J.J. Thomson conducted a quantitative study of cathode rays and was able to determine the value of the charge-to-mass ratio of particles emanating from the cathode. The value of this ratio does not depend on the cathode material or the residual gas in the cathode ray tube. $|e|/m = 1,759.10^{11}$ Coulombs/Kg.

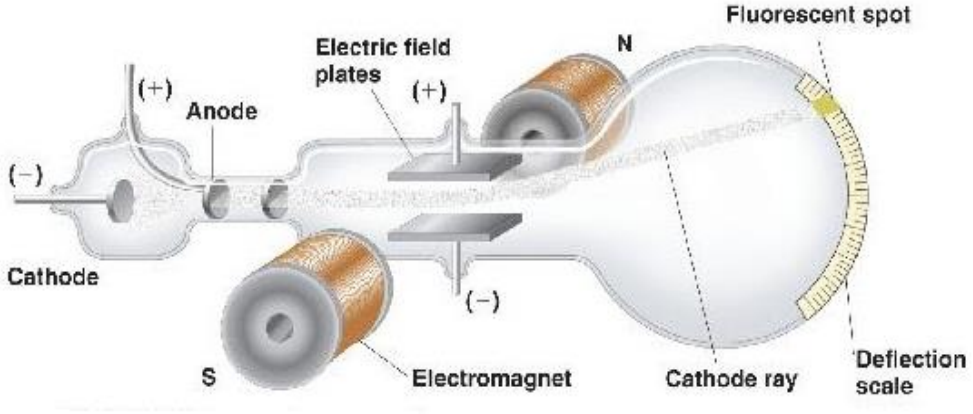


Figure II.4: J.J. Thomson's Experiment.

3.1.3. Millikan's Experiment (1868-1953)

The challenge of this experiment was to separately measure one of the two parameters, either the charge or the mass of the electron. To do this, Millikan sprayed tiny electrified oil droplets between the two horizontal electrodes of a charged parallel-plate capacitor. The principle of this experiment involved selecting a droplet and analyzing its motion under the influence of the forces acting on it.

Millikan, by simply measuring the speed as the ratio of the distance traveled over the time taken to traverse it for an oil droplet that he ionized by irradiating it with X-rays, experimentally observed that the ionization values were all integral multiples of $|e| = 1,592\times10^{-19}$ C, a constant that is now known as the elementary charge and is traditionally denoted as e;

This experiment turned out to be the first evidence of the quantization of electric charge, which is always a strictly integral multiple, positive or negative, of this fundamental value e.

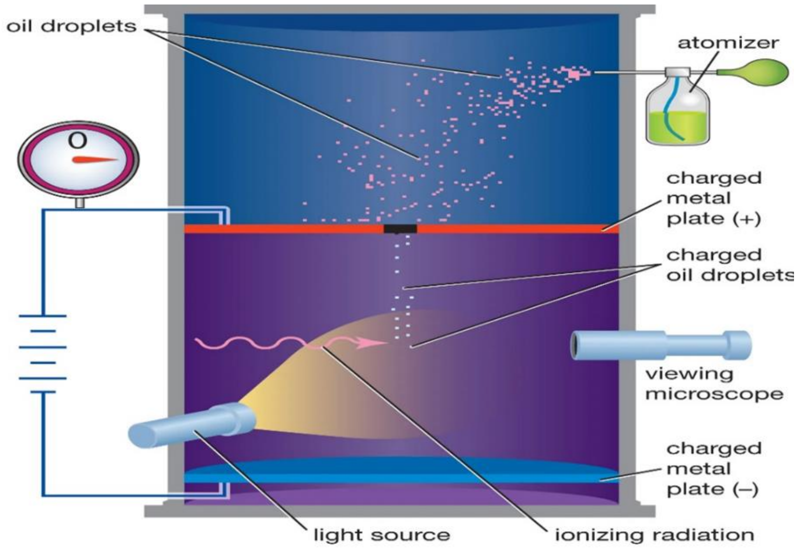


Figure II.5: Millikan's Experiment.

3.2. Nucleus

3.2.1. Identification

Rutherford's Experiment The experiment involves bombarding an extremely thin sheet of metal (gold) with radiation consisting of helium nuclei (He^{2+}).

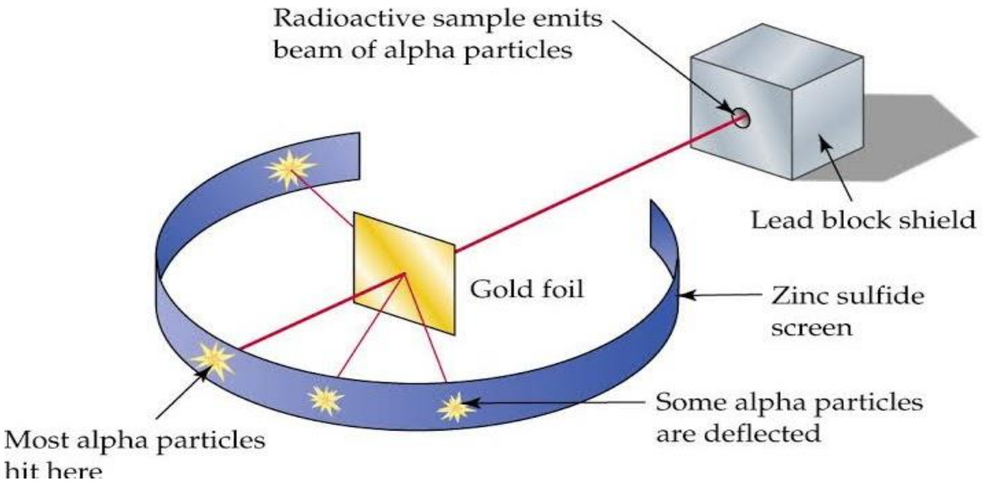


Figure II.6: Diagram of Rutherford's Experiment.

Interpretation:

By bombarding very thin sheets of gold with alpha particles, Hans Geiger and Ernest Marsden, who were students of Rutherford at the time, observed that a small fraction (1 in 8000) of these particles were deflected at large angles as if they were bouncing off a massive obstacle.

The impacts were observed in the dark under a microscope on a glowing screen of zinc sulfide. Rutherford concluded from this that the atom contained a massive core with a positive electric charge, capable of repelling the alpha particles.

3.2.2. Composition of the Atomic Nucleus

The nucleus is composed of stable elementary particles called nucleons, which exist in two forms when free: the neutron and the proton.

Protons have a positive charge: $q_p = +e = 1{,}602\times10^{-19}$ C

Proton mass: $m_p = 1{,}673\times10^{-27}$ kg ≈ 1836 m_{e-}

Neutrons have zero charge, and their mass is: $m_n = 1{,}675\times10^{-27}$ kg.

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

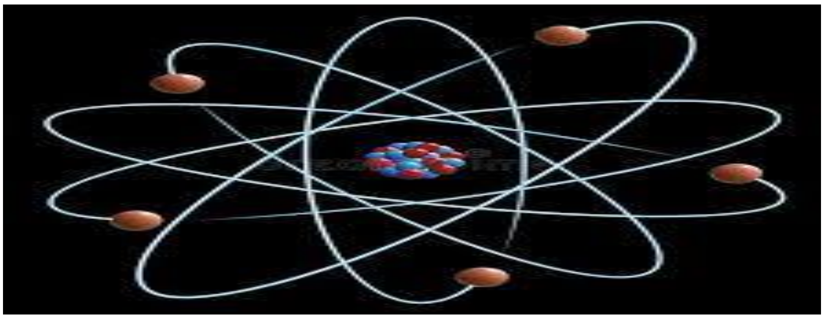


Figure II.7: Representation of an Atom.

3.2.3. Rutherford's Planetary Model

With these three fundamental particles: electron, proton, and neutron, we can construct a new model of the atom (an electrically neutral entity).

Rutherford's model. In this model, the atom consists of a nucleus, which contains almost all of its mass and is located at the center. It resembles the sun and contains a specific number of positively charged protons and neutrally charged neutrons, also known as nucleons, surrounded by negatively charged electrons (the planets).

The electrons (planets) orbit around the nucleus, forming an electron cloud. Electrical neutrality is due to the equality of the number of nuclear charges (protons) and electrons. This number, known as the atomic number, is denoted as Z.

Electrons are very lightweight, negatively charged particles, and they are denoted as (e^-), with e representing the elementary charge.

Nucleons include electrically neutral neutrons (n) and positively charged protons (p), each carrying a charge of +e.

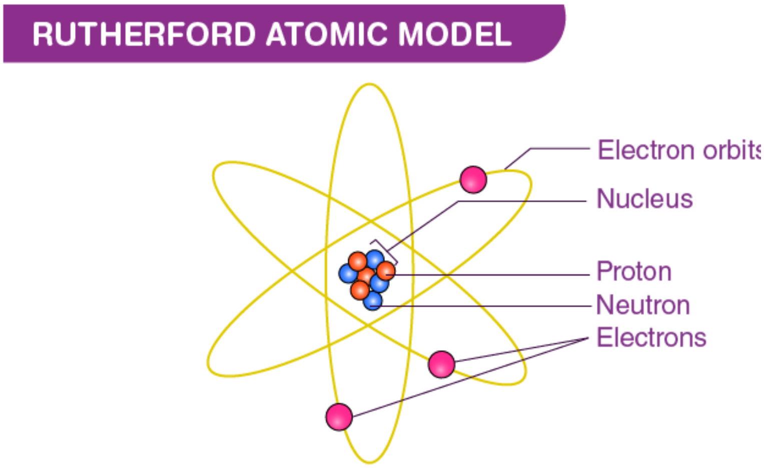


Figure II.8: Planetary Model (Rutherford) of the Atom.

3.2.4. Presentation and Characteristics of the Atom

Matter is composed of elementary units called atoms, and there are 112 atoms or elements that have been discovered, each of which is designated by its name and symbol. The atom X is characterized by two numbers:

Z: The charge number or atomic number, denoted as Z, represents the number of protons or electrons. For any element, the charge of the nucleus is +Z.e, and the charge of the electrons is -Z.e.

Therefore, Z = number of protons = number of electrons (provided that the element is neutral in its ground state).

A: The mass number, denoted as A, represents the number of nucleons (the sum of protons Z and neutrons N) with A = Z + N.

For any given element, the number of protons is fixed, but the number of neutrons can vary.

Note:

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

If the element is an anion (negative charge), we must add the charge number to the number of protons.

If the element is a cation (positive charge), we must subtract the charge number from the number of protons.

Example:

What is the number of protons, neutrons, and electrons that make up the composition of the following structures: ${}^{12}_{6}C$, ${}^{13}_{6}C$, ${}^{14}_{6}C\,{}^{18}_{8}O$, , ${}^{32}_{16}S^{2-}$, ${}^{27}_{13}Al^{3+}$, ${}^{16}_{8}O^{2-}$

Solution:

The composition of the atoms:

Element	Mass Number	Proton	Neutron	Electron
${}^{12}_{6}C$	12	6	6	6
${}^{13}_{6}C$	13	6	7	6
${}^{14}_{6}C$	14	6	8	6
${}^{18}_{8}O$	18	8	10	8
${}^{32}_{16}S^{2-}$	32	16	16	18
${}^{27}_{13}Al^{3+}$	27	13	14	10
${}^{16}_{8}O^{2-}$	16	8	8	10

4. Isotopes and Relative Abundance of Different Isotopes

4.1. Atoms and their Atomic Masses

There are two types of atoms: non-isotopic atoms and isotopes.

4.1.1. Non-Isotopic Atom

The atomic mass is equal to the sum of the masses of the atom's constituents:

$m_a = z \times m_{e^-} + m_N$

Z: Atomic number or charge number, representing the number of protons.

m_{e^-}: Mass of the electron

m_N: Mass of the nucleus

$mN = Z \times mp + n \times mn$

m_p: Mass of the proton

n: Number of neutrons

m_n: Mass of the neutron

4.1.2. Isotopes of a Chemical Element

Isotopes are atoms (nuclides) of the same chemical element with nuclei that have the same number of protons (Z) but different numbers of neutrons (N), resulting in different atomic mass numbers.

Example:

Natural hydrogen consists of three isotopes:

${}^{1}_{1}H$: hydrogen 1 electron + 1 proton + 0 neutron

${}^{2}_{1}H$: deuterium 1 electron + 1 proton + 1 neutron

${}^{3}_{1}H$: tritium 1 electron + 1 proton + 2 neutron

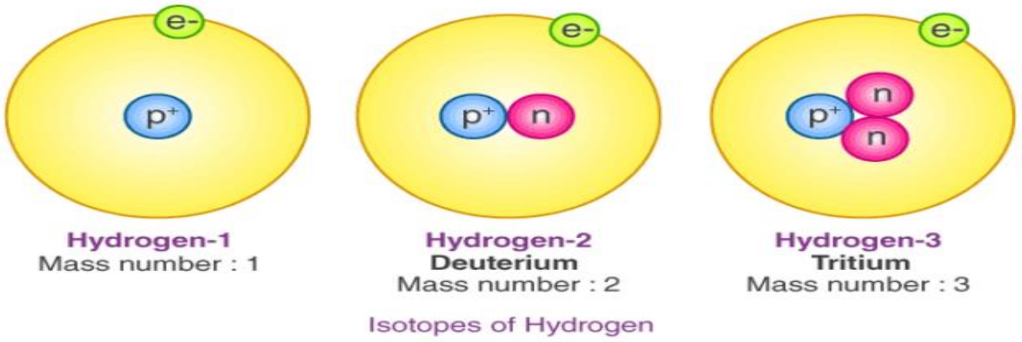


Figure II.9: Isotopes of Hydrogen.

Isotopes of Carbon:

Carbon-12 (12C) has three isotopes $^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$ with 6, 7, and 8 neutrons, respectively. Their natural abundances are 98.9%, 1.09%, and 0.01%, respectively.

Note:

The chemical properties of two isotopes of the same element are strictly the same because they are determined by the electron configuration, which is the same for both isotopes.

4.1.3. Relative Atomic Mass

In the general case, an element has one or more isotopes, so the atomic mass will be the sum of the relative proportions of each isotope.

$m = \Sigma (x_i . m_i)$ amu Similarly, the molar mass will be:

$M = \Sigma (x_i . M_i)$ (g/mol)

The atomic mass takes into account its composition and is given by the following equation:

$$\mathbf{m_a = \Sigma \alpha_i \times m_i / \Sigma \alpha_i}$$

α_i: Isotopic abundance or percentage

m_i: Atomic mass of the isotopes

Example:

Carbon has two stable isotopes with masses of 12 amu and 13 amu. The abundance of the latter is 1.1%. Calculate the atomic mass.

Solution :

$$m_a = \frac{\Sigma \alpha_i m_i}{\Sigma \alpha_i} = \frac{\alpha_1 x m_1 + \alpha_2 x m_2}{\alpha_1 + \alpha_2} \qquad \Sigma \alpha_i = 100\% \qquad \alpha_1 + \alpha_2 = 100\% \qquad \alpha_1 = 100\% - \alpha_2$$

$$m_a = \frac{(100\% - \alpha 2) x m_1 + \alpha_2 x m_2}{\alpha_1 + \alpha_2} = \frac{(m_2 - m_1) x \alpha 2 + 100 x m_1}{\alpha_1 + \alpha_2} = \frac{(13 - 12) x 1.1 + 100 x 12}{100}$$

$$m_a = 12.01 \text{ amu}$$

4.2. Mass Spectrometer: Bainbridge Spectrograph

To measure the mass of an atom in a mixture of isotopes, the most practical method is to measure the ratio q/m of an ionized atom (where **q** is the charge of the ion and **m** is its mass) using devices called "mass spectrometers." One example is the Bainbridge spectrograph. These mass spectrometers can separate the isotopes of an element and measure their abundances.

The Bainbridge spectrometer consists of four parts:

- An ionization source.
- A velocity filter.
- An analyzer.
- A detector.

An electron beam emitted by a heated filament positively ionizes the atoms of a gas. It receives ions moving at different velocities.

These ions are subjected to the simultaneous action of an orthogonal electric field and a magnetic field. Therefore, the ionic beam exiting the velocity filter is monocinetic.

In this part of the apparatus, an ion with mass m is subjected to a constant magnetic field with induction B directed perpendicular to its trajectory. The ion is then deflected in a circular path. The deflected ion impacts a photographic plate. The detector collects the ions and amplifies the signal, after which a computer system transforms the received information into a mass spectrum.

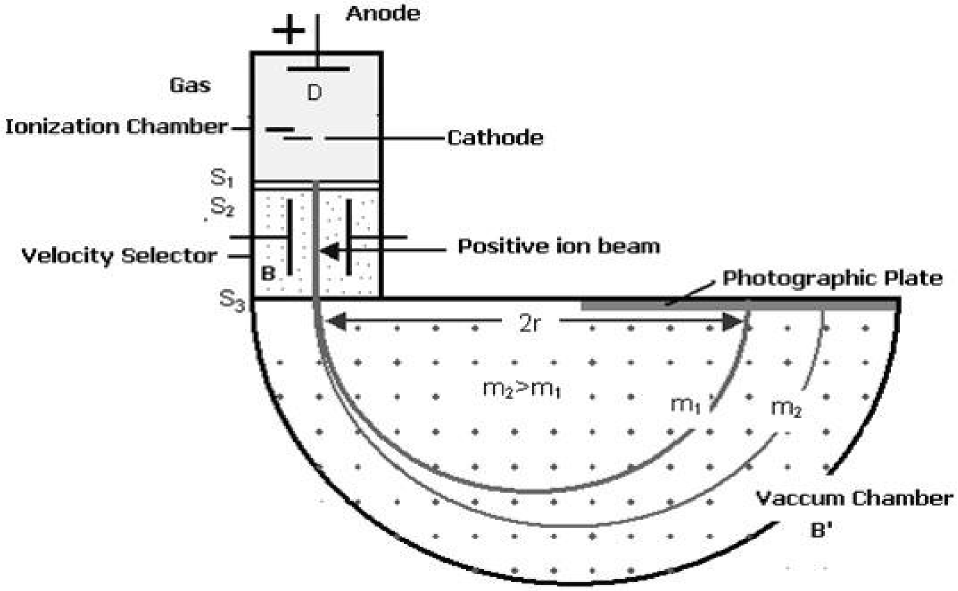


Figure II.10: Principle of the Bainbridge Spectrometer.

5. Binding and Cohesion Energy of Nuclei

5.1. Mass Defect

The formation of a nucleus from its separate nucleons is accompanied by a loss of mass Δm, also known as the mass defect. The mass defect Δm is always positive. Its expression is:

$$\mathbf{\Delta m = (Z \,.\, m_p + (A\text{-}Z) \,.\, m_n) - m_{nucleus}}$$

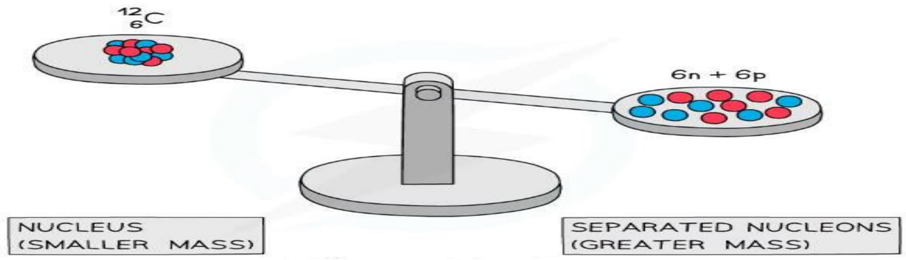


Figure II.11: Representation of a Mass Defect.

Example:

Determine the mass loss during the formation of the nucleus of uranium$^{235}_{92}\mathbf{U}$ from its nucleons.

Data: mp= 1,00728 a.m.u; mn= 1,00866 a.m.u, mU = 234,9942 a.m.u

Solution:

The nucleus of uranium-235 ($^{235}_{92}\mathbf{U}$) is composed of 92 protons and 143 neutrons.

Δm = (92. 1,00728 + 143. 1,00866) – 234,9942

Δm = 1,91394 a.m.u

5.2. Binding Energy

According to Einstein, the mass loss is transformed into energy that allows the nucleons to remain bound within the nucleus. $\mathbf{\Delta E = \Delta m.C^2}$

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

$\mathbf{E_b = \Delta m.C^2}$

$\mathbf{E_b}$: binding energy of the nucleus (in J, eV, or MeV)

Δm: mass defect of the nucleus (in kg) C: speed of light in a vacuum (m/s)

This energy is positive because it is received by the considered system (nucleus). An electronvolt is the energy gained by an electron under a potential difference of 1 volt.

1 eV = electron charge x potential difference = $1{,}6.10^{-19}$ C.1V

1eV = $1{,}6.10^{-19}$ joules and 1MeV = 10^6 eV

Energy of one atomic mass unit (amu):

E= Δm .C^2 Where: The mass of 1 amu =$1{,}66056.10^{-27}$ Kg

$\Delta m= 1u = 1,66.10^{-27}$ Kg

$E=1,66.10^{-27}. (3.\ 10^{8})^{2}=14,94.10^{-11}$ J

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

$E=14,94.10^{-11}/1,6.10^{-19}= 933,\ 75\ .10^{6}$ eV = 933,75 MeV

Example

The mass of the ${}^{4}_{2}He$ nucleus is 4.0026 u. Knowing that the masses of the proton and neutron are: $m_n = 1,0086$ u ; $m_p = 1,0073$ u.

Calculate the mass defect and the binding energy (in J and MeV) of the helium nucleus.

Solution:

The mass defect of the helium-4 nucleus and the corresponding energy in MeV:

The mass defect Δm: $\Delta m = (Z.\ mp + N.\ mn) - ({}^{4}{}_{2}He)$

$\Delta m = (2 \times 1,0073 + 2 \times 1,0086) - 4,0026$; $\Delta m = 0,0292\ u.$

The corresponding energy in MeV You can convert from a.m.u to MeV by multiplying a.m.u by 933.75.

So : ΔE= 0,0292 x 933,75= 27,2655 MeV

Otherwise, we convert and calculate the energy using the formula

$\boldsymbol{\Delta E} = \boldsymbol{\Delta m} \times \boldsymbol{c^2}$ with Δm in [Kg] and c in $[m.s^{-1}]$

$\Delta E = \Delta m \times c^2 = 0,0292 \times 1,66 \times 10^{-27} \times (3 \times 10^8)^2 = \mathbf{0,\ 4368 \times 10^{-11}\ J}$

$\Delta E = 0,4368 \times 10^{-11}\ J = 0,4368 \times 10^{-11}\ 1,6 \times 10^{-13} = 0,273\ .\ 10^2 = 27,3\ Mev.$

5.3. Cohesion Energy

The current explanation of cohesion energy can be further elaborated. Cohesion energy, often referred to as binding energy (E_b), is the amount of energy required to disassemble a nucleus into its individual protons and neutrons. It represents the energy that holds the nucleus together. This energy is typically negative, indicating that work must be done to break the nucleus apart. It is related to the total nuclear energy (E) by the equation:

$\mathbf{E_b = -E}$

Where:

$\mathbf{E_b}$: represents the binding energy, i.e., the energy required to break the nucleus into free nucleons.

E: represents the total nuclear energy, which is negative due to the attractive forces that bind the nucleons together.

This negative sign reflects the fact that energy must be supplied to overcome the attractive nuclear forces. The stronger the nuclear cohesion, the more negative the energy and the higher the stability of the nucleus.

6. Nuclear Stability

6.1. Binding Energy per Nucleon

Aston Curve: The Aston curve illustrates how the binding energy per nucleon varies with the mass number of different nuclei. It is a crucial tool in nuclear physics for comparing nuclear stability. The binding energy per nucleon is defined as the total binding energy Eb divided by the number of nucleons (A). It is expressed in MeV/nucleon.

The curve shows that:

Light nuclei (low mass numbers) tend to increase their stability via fusion (combining to form heavier nuclei with higher binding energy per nucleon).

Heavy nuclei (high mass numbers) increase stability through fission (splitting into smaller nuclei).

The most stable nuclei are found near iron (Fe), where the binding energy per nucleon reaches a maximum, approximately 8 MeV/nucleon. This maximum indicates a highly stable configuration, explaining why fusion and fission both release energy: they lead to products with higher binding energy per nucleon.

Examples*:*

For uranium ^{238}U: E_b /A= 7,57 MeV per nucleon.

For iron ^{56}Fe: E_b /A= 8,79 MeV/ per nucleon.

Iron ^{56}Fe is more stable than uranium ^{238}U.

The Aston curve below shows the variation of Eb per nucleon (A) as a function of the number A of the nucleon.

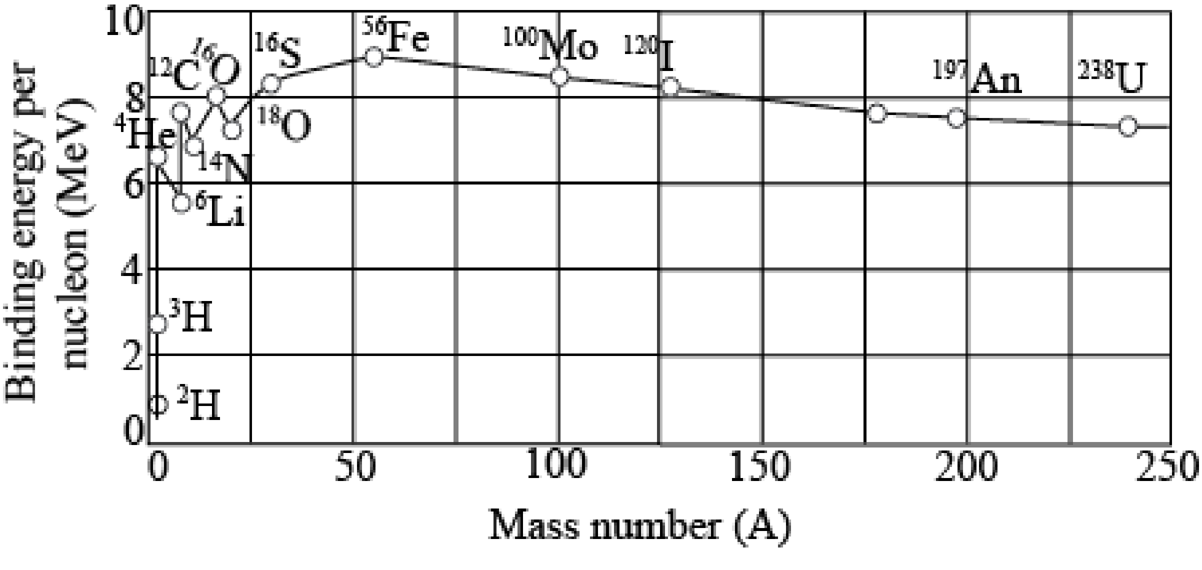


Figure II.12: Aston Curve.

6.2. The Zone of Stability

According to Rutherford, the atom is mainly composed of empty space, and all its mass is concentrated in the nucleus, which consists of protons and neutrons.

Therefore, the stability of a nuclide is influenced by the number of protons and neutrons. This effect is represented by a stability diagram (see Figure II.13) that shows the variation of the number of neutrons as a function of the atomic number Z in nuclei.

The shape of this curve clearly shows that stability is:

- significant for all elements with Z=N (represented by the diagonal);
- less significant (less stable) for 20≤ Z≤84, where N>Z;
- very low, meaning that the nuclei are highly unstable, for Z≥ 84, as they are radioactive (α emission).

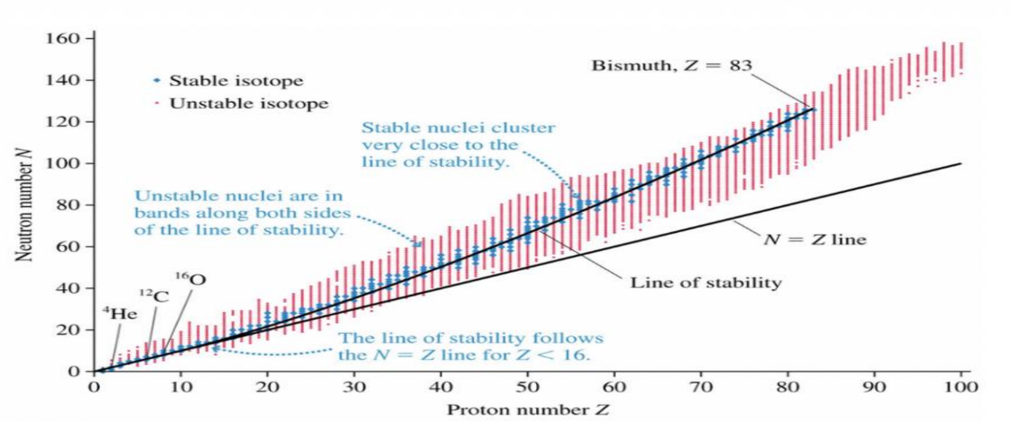


Figure II.13: Isotope Stability Diagram

For the first elements with Z < 30, we observe that stable isotopes have a number of neutrons roughly equal to that of protons, Z ≈ n.

Example 1:

$^{51}_{23}V$: Z= 23 et n =28.

Beyond Z = 30, stable isotopes have a higher number of neutrons than protons: n > Z.

Example 2:

$^{75}_{33}As$ Z= 33, where Z = 33 and n = 42.

Note: As the number of protons increases, the number of neutrons must also increase for the nuclide to be stable.

Example 3:

1. Calculate the energy in MeV of the nucleons in the nucleus of the helium isotope $^{6}{}_{2}He$, knowing that its mass is 6.018900 amu.

2. The mass of the isotope $^{4}{}_{2}He$is 4.001503 amu. Which isotope is more stable?

Solution:

Deficiency in mass:

Δm = (Z × mp + (A - Z) × mn) - m_nucleus

Δm = (2 x 1, 0072765 + 4 x 1, 0086649) – 6.0189 = 0, 0303126 amu. 1,66. 10^{-27}= 0,0503. 10^{-27}Kg.

Binding energy per nucleon:

E= Δm.C^2=0,0503. 10^{-27}. $(3.108)^2$= 0,4527. 10^{-11}joul/1,66.10^{-19}=0,283. 10^8 eV=28,3 MeV/nucleus.

Or using the second method:

E = 0, 0303126 amu. 933,75 = 28.3 MeV/nucleus.

Binding energy per nucleon for $^{6}_{2}\mathbf{He}$: $E_{nucleus}$/A = 28.3 / 6 = 4.716 MeV/nucleon.

To compare the stability of the two isotopes, we need to calculate the binding energy per nucleon for $^{4}_{2}\mathbf{He}$ using the same method. Once we have both values,

we can determine which isotope is more stable. The isotope with the higher binding energy per nucleon is more stable. The binding energy per nucleon:

$E_{nucleus}$/A = 28.3/6 = 4.716 MeV/nucleon.

The mass of the isotope $^{4}_{2}\mathbf{He}$ is 4.001503 atomic mass units (amu)

To determine which isotope is more stable, we can calculate their binding energies per nucleon **(E_{bond}/A).**

For helium $^{4}_{2}\mathbf{He}$: Δm = (2 x 1.0072765 + 2 x 1.0086649) – 4.001503 = 0.0303798 amu

E_{bond} = 0.0303798 x 933,75 = 28.34 MeV

E_{bond} /A = 28.34/4 = 7.08 MeV/nucleon

The rule states that "Nuclei with the highest binding energy per nucleon are the most stable."

According to the binding energy per nucleon curve (E_{bond} /A = f(A)), the most stable zone is where 7.5 < E_{bond} /A < 8.8 MeV.

Based on the calculated E_{bond} /A values, we can conclude that helium $^{4}_{2}\mathbf{He}$ is more stable compared to helium $^{6}_{2}\mathbf{He}$.

Corrected Exercises

Exercise 1: Check the correct answer(s).

1. An atom

a- is electrically neutral
b- has as many neutrons as protons.
c- has as many protons as electrons
d- has as many neutrons as electrons

2. a proton

a- carries an electric charge equal in absolute value to that of the electron.
b- has the same electrical charge as a neutron.
c- has the same mass as a neutron.
d- has the same mass as the electron.

3. The mass of an atom is approximately equal to

a- the mass of its protons
b-the mass of its nucleons
c- the mass of its neutrons
d -the mass of its nucleus

4. An atom and an ion belong to the same chemical element if they have

a- the same atomic number Z
b- the same number of nucleons A
c- the same number of protons
d- the same number of neutrons

5- isotopes

a- belong to the same chemical element
b-have the same number of neutrons
c-have the same number of nucleons
d- have the same number of protons

Exercise 2:

Give the constitution (number of protons, neutrons and electrons) of the following atoms and ions: ${}^{238}_{92}\mathrm{U}$, ${}^{222}_{86}\mathrm{Rn}$, ${}^{24}_{12}\mathrm{Mg}$, ${}^{24}_{12}\mathrm{Mg}^{2+}$, ${}^{52}_{24}\mathrm{Cr}^{3+}$ ${}^{127}_{53}\mathrm{I}^{-}$.

Exercise 3:

Let an iron atom (Z = 26 and A = 56):

a. Determine, approximately, the mass of an iron atom.
b. Find the number of iron atoms present in an iron nail weighing 12 g.

Data: Mass of a nucleon: $m=1.7\times10^{-27}$ kg.

Exercise 4:

Let's assume that the mass of the aluminum atom ${}^{27}_{13}\mathrm{Al}$. is equal to the sum of the masses of the particles that make it up

1. What is the mass of the nucleus of an aluminum atom?

2. What is the mass of the electron chain of an aluminum atom? Compare.
3. What is the mass of an aluminum atom?

Data: m_{proton} =1,673 10^{-27} kg, m_{neutron} = 1,675 10^{-27} kg, m_{electron} =9,109 10^{-31} kg.

Exercise 5:

Consider an unknown atomic nucleus with an electrical charge q=928 10^{-20} coulomb, knowing that the mass of one mole of this nucleus is m=141.103 g.

Give the constitution of this nucleus and the symbolic representation of the corresponding atom.

Exercise 6:

Consider the phosphorus atom, symbol P, with 15 electrons and one more neutron than protons.

1. What is the atomic number of this element?
2. Calculate its neutron number.
3. Give its symbolic representation.
4. Calculate the electric charge carried by the nucleus of this atom.
5. Calculate the electric charge carried by the phosphorus atom.
6. Give the mass of a phosphorus atom.

Exercise 7:

We have one milliliter of liquid water. Calculate:

1. The corresponding mass of water.
2. The number of gram-molecules of water.
3. The number of water molecules.
4. The number of moles of oxygen and hydrogen atoms contained in the water.
5. The number of gram-atoms of oxygen and hydrogen contained in the water.
6. The number of oxygen and hydrogen atoms contained in the water.

Data: (H_2O) = 1g/cm^3, M (H_2O) = 18 g/mol, Avogadro's number N=6.023×10^{23}.

Exercise 8:

Natural copper is made up of two different isotopes. The mass of each is 62.929 and 64.927 respectively. The atomic number of copper is Z=29.

a- Give the composition of the two isotopes.

b- Knowing that the atomic mass of the natural mixture formed by the two isotopes is 63.54. Calculate the abundance of each isotope.

Exercise 9:

The nucleus of the lithium atom is made up of 4 neutrons and three protons.

a. Calculate the theoretical mass of this nucleus in amu. Compare it with its real value of 7.01601 amu.

b. Calculate the cohesion energy of this nucleus in J and MeV.

Data: mp=1.00727 amu, mn=1.00866 amu, C= 3 .10^8 m/s, 1ev=1.6 10^{-19} J.

Exercise 10:

Calculate the binding energy per nucleon in MeV of the following oxygen isotopes (Z=8) ^{16}O (15.9949 amu), ^{17}O (16.9991 amu), ^{18}O (17.9992 amu).

Which of the three is more stable.

Data: mp=1.00727 amu, mn=1.00866 amu.

Correction

Exercise 1:

1. a and c.
2. a and c.
3. b and d.
4. a and c.
5. a and d.

Exercise 2:

The structure of atoms and ions:

	N° of proton	N° of neutron	N° of electron
$^{238}_{92}U$,	92	146	92
$^{222}_{86}Rn$,	86	136	86
$^{24}_{12}Mg$,	12	12	12
$^{24}_{12}Mg^{2+}$,	12	12	10
$^{52}_{24}Cr^{3+}$	24	28	21
$^{127}_{53}I^{-}$.	53	74	54

Exercise 3:

a. Approximate Mass of an Iron Atom

The mass of an iron atom is primarily due to its nucleons (protons and neutrons), as the mass of electrons is negligible. The total mass of an iron atom is approximately:

Mass of one iron atom=A× Mass of one nucleon;

Mass of one iron atom=$56\times1.7\times10^{-27}$ kg;

Mass of one iron atom=9.52×10^{-26} kg.

b. Number of Iron Atoms

The molar mass of iron is approximately 56 g/mol. To find the number of moles of iron in the nail:

Number of moles= $\frac{\text{Mass of iron nail}}{\text{Molar mass of iron}}$

Number of moles= $\frac{12\text{ g}}{56\text{ g/mol}}$ =0.2143 mol.

Using Avogadro's number, the number of atoms is: Number of moles × N_A

Number of atoms=$0.2143\times6.023\times10^{23}$.

Number of atoms=1.29×10^{23} atoms.

Exercise 4:

1. The mass of the nucleus of the aluminum atom

$m_{\text{nucleus}}=m_{\text{protons}}+m_{\text{neutrons}}$

$m_{\text{nucleus}} = Z\times m_p + N\times m_N$ (Z = 13 and N = 14)

$m_{\text{nucleus}}=13\times1.673\times10^{-27}+14\times1.675\times10^{-27}$

$m_{\text{nucleus}}=45.2\times10^{-27}$ kg.

2. The mass of the electron cloud of the aluminum atom

$m_{\text{electrons}} = Z\times m_e = 13\times9.109\times10^{-31}$

$m_{\text{electrons}} = 118.417\times10^{-31}$ kg $= 0.0118\times10^{-27}$ kg.

The mass of the electrons is negligible compared to the mass of the nucleus.

3. The mass of the aluminum atom

$m_{\text{atom}} = m_{\text{nucleus}} + m_{\text{electrons}} \approx m_{\text{nucleus}} = 45.2\times10^{-27}$kg.

Exercise 5:

Charge of a nucleus = charge of protons + charge of neutrons:

$q_{\text{nucleus}}=q_{\text{protons}}+q_{\text{neutrons}}$ (q_{neutrons}=0C)

$q_{\text{nucleus}} = q_{\text{protons}} = Z\times e = 9.28\times10^{-20}$ coulomb (e=1.6×10^{-19}C)

$Z=\frac{q}{e}=\frac{9.28\times10^{-20}}{1.6\times10^{-19}}$ =5 8, so the number of protons is 58.

We also have: $m_{\text{nucleus}} = m_{\text{protons}} + m_{\text{neutrons}}$

$m_{\text{nucleus}} = Z\times m_p + N\times m_N$

$N = \frac{m_{nucleus} - Z \times m_p}{m_N}$

For 1 mole, 6.023×10^{23} atoms weigh 141.103 g:

For 1 atom, the mass is: $\frac{141.103}{6.023 \times 10^{23}} = 23.4273 \times 10^{-23}$ g $= 23.4273 \times 10^{-26}$ kg $= 234.273 \times 10^{-27}$ kg.

$N = \frac{234.273 \times 10^{-27} - 58 \times 1.673 \times 10^{-27}}{1.675 \times 10-27} = 82$

The symbolic representation of the atom is: ${}^{140}_{58}X$

Exercise 6:

1. The atomic number of this element

The atomic number of an element corresponds to the number of protons in its nucleus. Since the phosphorus atom has 15 electrons and is neutral, it must also have 15 protons. Therefore: Atomic number of phosphorus = 15.

2. Calculate its neutron number

We are told that the phosphorus atom has one more neutron than protons. Since it has 15 protons, the number of neutrons is: 16 neutrons

3. The symbolic representation

The symbolic representation of an atom includes its atomic number (Z) and its mass number (A, which is the sum of protons and neutrons). For phosphorus with 15 protons and 16 neutrons:
Mass number (A) = 15 protons + 16 neutrons = 31
The symbolic representation is: ${}^{31}_{15}P$

4. **Calculate the electric charge carried by the nucleus of this atom.**

The electric charge of the nucleus is due to the protons, as neutrons have no charge. The charge of each proton is the elementary charge (e), which is 1.6×10^{-19}C.
The total electric charge of the nucleus is:
Charge of nucleus=Number of protons×e=$15 \times 1.6 \times 10^{-19}$ C
Charge of nucleus=2.4×10^{-18} C

5. Calculate the electric charge carried by the phosphorus atom.

For a neutral phosphorus atom, the total electric charge is the sum of the charges of the protons and electrons. Since the number of protons equals the number of electrons in a neutral atom, the net electric charge is zero (0 C).

6. The mass of a phosphorus atom.

The mass of an atom is the sum of the masses of its protons, neutrons, and electrons. The mass of an electron is negligible compared to the mass of protons and neutrons, so we only consider the protons and neutrons.

For phosphorus with 15 protons and 16 neutrons:

Mass of phosphorus atom=15×mp+16×mN

Mass of phosphorus atom=$15\times1.673\times10^{-27}+16\times1.675\times10^{-27}$kg

Mass of phosphorus atom=5.1895×10^{-26}kg

Exercise 7:

1. The corresponding mass of water

The mass mmm is given by: $m=\rho\cdot V=1\ \frac{g}{cm^3}\ \cdot 1cm^3=1g$

The mass of water is **1 g**.

2. The number of gram-molecules of water

The number of moles n is given by: $n=\frac{m}{M}$

$n=\frac{1g}{18g/mol}\ = 0.0556mol.$

The number of gram-molecules of water is 0.0556 mol.

3. The number of water molecules

The number of water molecules N is given by: $N=n\cdot N_A$

$N=0.0556\cdot6.023\times10^{23} = 3.35\times10^{22}$ molecules

The number of water molecules is 3.35×102^{23}.

4. The number of moles of oxygen and hydrogen atoms

Each molecule of H_2O contains 1 oxygen atom and 2 hydrogen atoms. Therefore:

$n(O)=n(H_2O) = 0.0556mol.$

$n(H) = 2\cdot n(H_2O) = 2 \text{ x } 0.0556= 0.1112$ mol.

5. The number of gram-atoms of oxygen and hydrogen

The number of gram-atoms is equivalent to the number of moles:

- Gram-atoms of oxygen: 0.0556 mol.
- Gram-atoms of hydrogen: 0.1112 mol.

6. The number of oxygen and hydrogen atoms

The number of atoms is given by:

$N(O)=n(O)\cdot NA=0.0556\cdot 6.023\times10^{23} = 3.35\times10^{22}$ atoms.

$N(H)=n(H)\cdot NA=0.1112\cdot 6.023\times10^{23} = 6.70\times10^{22}$ atoms.

Exercise 8:

a. The composition of the two isotopes:

Isotope 1: $m_1= 62,929 \approx 63$

$^{63}_{29}Cu$ 29 protons, 29 electrons; 34 neutrons

Isotope 2: $m_2=64,927 \approx 65$

$^{65}_{29}Cu$ 29 protons, 29 electrons; 36 neutrons

b. **The abundance of each isotope**.

$m = \sum \tau_i \; m_i$ We have 2 isotopes $\Longrightarrow m_{Cu} = \tau_1 m_1 + \tau_2 m_2$

With ; $m_{cu} = 63,54$

$m_1 = 62,929$

$m_2 = 64,927$

τ_i: abundance of isotope

$$\begin{cases} m_{Cu} = \tau_1 m_1 + \tau_2 m_2 \\ \tau_1 + \tau_2 = 100\% = 1 \Longrightarrow \tau_1 = 1 - \tau_2 \end{cases} \Longrightarrow \begin{cases} m_{Cu} = (1 - \tau_2)\, m_1 + \tau_2 m_2 \\ \tau_1 = 1 - \tau_2 \end{cases}$$

$\tau_2 = 0,3058 = 30,58\%$

$\tau_1 = 0,6942 = 69,42\ \%$

Exercise 9:

1. **The theoretical mass of the nucleus.**

$m_{\text{theoretical}} = Z\, m_p + N\, m_N \Longrightarrow m_{\text{theoretical}} = 4 \times 1,00866 + 3 \times 1,00727$

$m_{\text{theoretical}} = 7,05645$ amu

The given real mass $m_{\textbf{real}} = 7,01601$ amu

$\Delta m = 7,05645 - 7,01601 = 0,04044$ amu

2. **The binding energy of this nucleus.**

First method: $\Delta E = \Delta m\, C^2 = 0,04044\ 1,66.\ 10^{-27}\, (3 \times 10^8)^2 = 6,0417\ 10^{-12}$ Joule

$\Delta E = 6,0417\ 10^{-12}$ Joule $= 6,0417\ 10^{-12} / 1,6\ 10^{-19}$ ev $= 3,77\ 10^7$ ev

$\Delta E = 3,77\ 10^7$ ev $= 3,77\ 10^7 / 10^6$ Mev $= 37,7$ Mev.

Second method: 1 amu $\longrightarrow$ **933 Mev**

0,04044 amu $\longrightarrow$ ΔE? Mev

$\Delta E = 0{,}04044 \times 933 = 37{,}7$ Mev $= 6{,}0417\ 10^{-12}$ Joule $= 37{,}7$ Mev.

Exercise 10 :

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

$\Delta m = (Z \times mp + (A - Z) \times mn) - m_{\text{nucleus}}$

^{16}O $\Delta m= (8 \times 1{,}00727 + 8 \times 1{,}00866) - 15{,}9949 = 0{,}1325$ amu

^{17}O $\Delta m= (8 \times 1{,}00727 + 9 \times 1{,}00866) - 16{,}9991= 0{,}137$ amu

^{18}O $\Delta m= (8 \times 1{,}00727 + 10 \times 1{,}00866) - 17{,}9992= 0{,}1455$ amu

1 amu $\longrightarrow$ 933 Mev

^{16}O $\Delta E= 0{,}1325 \times 933 = 123{,}6598$ Mev

^{17}O $\Delta E= 0{,} 137 \times 933 = 127{,}821$ Mev

^{18}O $\Delta E= 0{,} 1455 \times 933 = 135{,}8074$ Mev

To determine the most stable isotope, we calculate $\Delta E/A$:

^{16}O $\Delta E/A= 123{,}6598 /16 = 7{,}7287$ Mev

^{17}O $\Delta E/A= 127{,}821 /17 = 7{,}5188$ Mev

^{18}O $\Delta E/A= 135{,}8074 /18= 7{,}5448$ Mev

The most stable isotope is ^{16}O because its binding energy per nucleon ($\Delta E/A$) is the highest.

Chapter III: Nuclear Reactions

1. Introduction

The relationship between the number of protons and the number of neutrons is the primary factor that determines the stability or instability of a given nuclide.

This fact can be explained simply by considering that positively charged protons repel each other, and the addition of neutrons stabilizes nuclides by a "dilution" effect of positive charges. When the protons' number becomes too high ($Z > 84$), this "charge dilution" effect becomes ineffective because Z is too high, and there are no longer stable nuclei.

For $A-Z / Z > 1.5$, the element is generally radioactive.

During a nuclear reaction, the number of charge Z and the mass number A are conserved.

Radioactivity: is a spontaneous nuclear transformation that alters the composition of the atomic nucleus and, consequently, the nature of the atom.

The transformation of one nucleus into another nucleus is called: radioactive transmutation.

Two types of transmutations are distinguished:

- ✓ Spontaneous: Natural radioactive decay (radioactivity exhibited by natural nuclides);
- ✓ Induced: Artificial radioactivity.

2. Natural Radioactivity

Natural radioactivity results from the instability of the nuclei of certain natural elements.

It involves the spontaneous disintegration of the nucleus, resulting in a radioactive or stable nucleus and various radiations. Some nuclides are unstable because their combination of protons and neutrons form a fragile architecture. They have a certain probability of decaying, meaning they spontaneously and abruptly change their structure.

This modification is accompanied by nuclear reactions that cannot be altered by any external intervention (temperature, pressure, etc.).

These nuclei can spontaneously disintegrate by expelling certain components to form more stable nuclei. These radioactive elements were discovered by Becquerel in 1896.

There are three different forms of radioactivity:

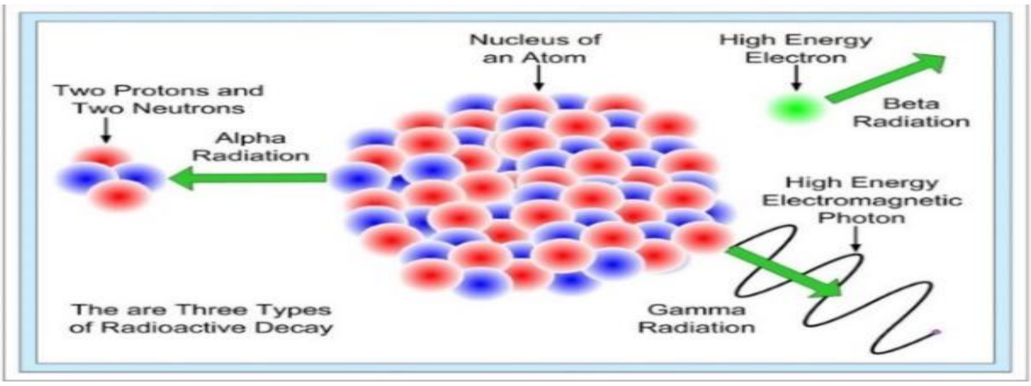


Figure III.1: Types of radioactive decay.

2.1 Alpha Radiation α: (${}^{4}_{2}He$)

This type of radiation typically involves heavy atoms with Z>83 and is characterized by the emission of alpha particles, which are ${}^{4}_{2}He$ nuclei. In this case, both the number of protons and neutrons are altered simultaneously by the emission of alpha particles, as indicated in the radioactive decay reaction below:

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

To correctly write a radioactive decay reaction, one must verify Soddy and Fajans' law, which states the conservation of:

- Mass number (A of both sides must be equal);
- Atomic number (Z of both sides must be equal).

Examples:

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

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

- The nucleus of helium is also called alpha radiation in common usage;
- This radiation is not very dangerous because a few millimeters of paper are sufficient to stop it.
- This radioactivity only concerns heavy nuclei, usually with atomic numbers greater than 74 (tungsten). The heaviest nucleus affected by this radioactivity is uranium-238.

2.2 Beta Radiation

There are two types of beta radiation: β^- (electron) and β^+ (positron).

2.2.1 β^- Radiation

Concerns unstable isotopes with an excess of neutrons, emitting electrons.

These nuclides seek to stabilize by increasing the number of protons (P) and decreasing the number of neutrons (n), as shown in the reaction below:

$${}^{1}_{0}n \longrightarrow {}^{0}_{-1}e + {}^{1}_{1}P + \bar{\upsilon}$$

Where $\bar{\upsilon}$ represents the anti-neutrino.

$${}^{A}_{Z}X \longrightarrow {}^{A}_{Z+1}Y + {}^{0}_{-1}e + \bar{\upsilon}$$

The nuclide X is called the "parent nucleus," and the nuclide Y is the " daughter nucleus." X and Y correspond to different chemical elements.

The antineutrino ensures the conservation of momentum and energy.

Example:

$${}^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{\;0}_{-1}\text{e} + \bar{\upsilon}$$

2.2.2 β⁺ Radiation

This type of radiation concerns unstable elements that have an excess of protons and emit positrons (β^+, ${}^{\;0}_{+1}\text{e}$). Positrons have the same mass as electrons but different charges.

These nuclei seek to stabilize by increasing the number of neutrons and decreasing the number of protons, which means the protons transform into neutrons, as shown in the following

$${}^{1}_{1}\text{P} \longrightarrow {}^{\;0}_{+1}\text{e} + {}^{1}_{0}\text{n} + \upsilon$$

radioactive reaction: where: υ: neutrino

$${}^{A}_{Z}\text{X} \longrightarrow {}_{Z-1}^{\;\;\,A}\text{Y} + {}^{\;0}_{+1}\text{e} + \upsilon$$

X and Y correspond to different chemical elements. The particle labeled ${}^{0}{}_{+1}\text{e}^{-}$ is a positron (or anti-electron) with the same mass as the electron but opposite charge. The neutrino ensures the conservation of momentum and energy.

Example:

$${}^{14}_{8}\text{O} \longrightarrow {}^{14}_{7}\text{N} + {}^{\;0}_{+1}\text{e} + \upsilon$$

- When a nucleus is formed during a decay (α or β), it is in an excited state.
- Returning to the ground state releases a photon (energy) of the δ type.

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

2.3 Gamma radiation

Is pure electromagnetic radiation, so it has no mass or charge, but it is highly energetic and of the same nature as light (it's a photon), but it has very short wavelengths in a vacuum.

Example:

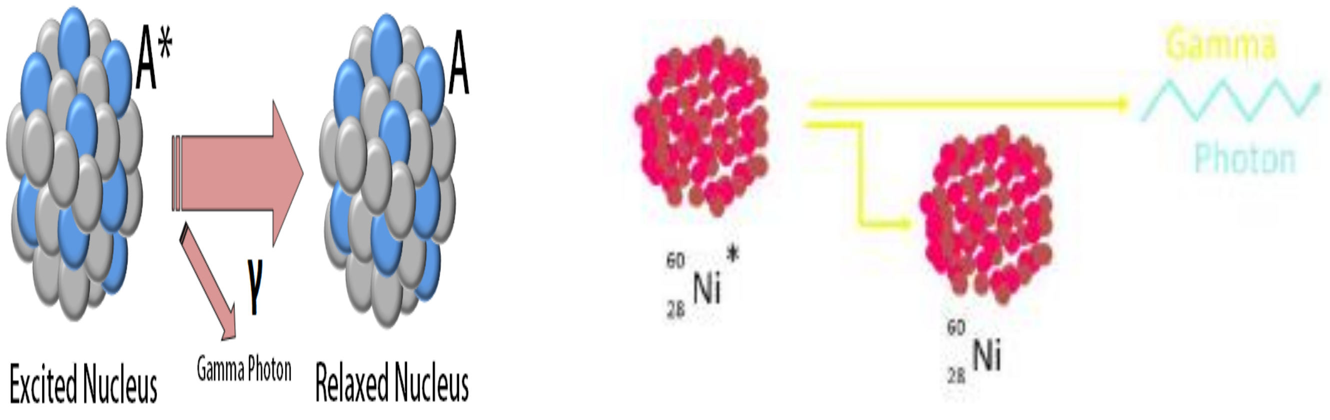


Figure III.2: Gamma rays.

3. Artificial radioactivity and nuclear reactions

This is artificial radioactivity in certain nuclei resulting from human intervention. The first artificial radioactive nuclei were obtained by Rutherford in 1919 by bombarding nitrogen atoms with alpha particles, leading to the formation of new nuclei.

$$^{14}_{7}N + \,^{4}_{2}He \longrightarrow \,^{1}_{1}P + \,^{17}_{8}O$$

There are three types of nuclear reactions:

a. Nuclear fission;
b. Nuclear fusion;
c. Transmutations.

3.1. Nuclear Fission

Atoms with very high mass numbers (A), when bombarded with neutrons, can undergo a break, resulting in lighter atoms and the regeneration of neutrons.

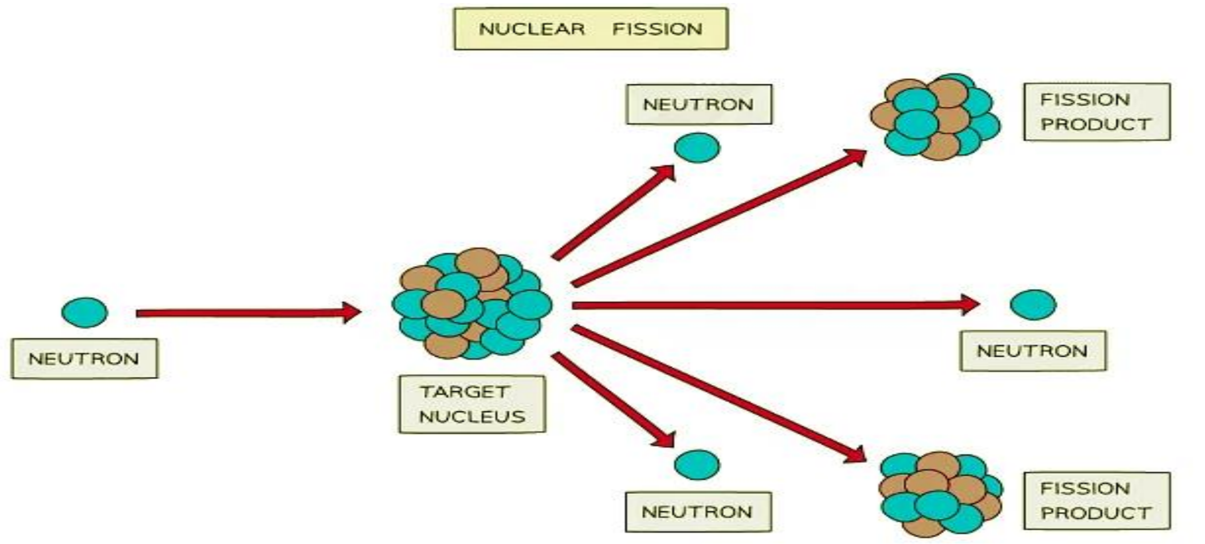


Figure III.3: Nuclear Fission.

Examples:

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

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

3.2. Nuclear Fusion

During this type of reaction, two light nuclei will fuse to form a heavier atom and various other particles.

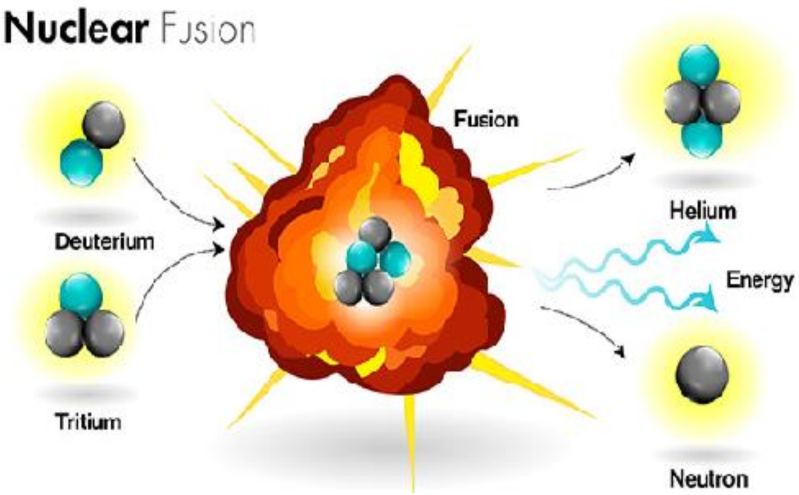


Figure III.4: Nuclear Fusion.

Examples

$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{1}e$

${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n$

3.3. Transmutation

These reactions produce nuclides with a mass number equal to or very close to that of the target nuclide. The formed nuclides can be stable or radioactive.

Example:

${}^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n$

Abbreviated notation for this reaction: ${}^{27}_{13}Al\ (\alpha, n)\ {}^{30}_{15}P$

Example of application:

Complete the following nuclear reactions. For each equation, indicate the type of reaction it represents:

${}^{131}_{53}I \longrightarrow {}^{131}_{52}Te + \cdots$

${}^{124}_{53}I \longrightarrow \ldots + \beta^-$

${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{1}_{0}n + \ldots$

${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{16}_{8}O + \cdots$

${}^{215}_{84}Po \longrightarrow {}^{211}_{82}Pb + \cdots$

${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{139}_{53}I + 3\,{}^{1}_{0}n + \ldots$

${}^{9}_{4}Be\ (\beta^+, \alpha) \ldots$

Solution:

${}^{131}_{53}\mathrm{I} \longrightarrow {}^{131}_{52}\mathrm{Te} + {}^{0}_{1}\mathbf{e}$ (β^+ decay)

${}^{124}_{53}\mathrm{I} \longrightarrow {}^{124}_{54}\mathbf{Xe} + \beta^-$ (β^- decay)

${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{1}_{0}\mathrm{n} + {}^{4}_{2}\mathbf{He}$ (Nuclear fusion)

${}^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{16}_{8}\mathrm{O} + {}^{2}_{1}\mathbf{H}$ (Transmutation)

${}^{215}_{84}\mathrm{Po} \longrightarrow {}^{211}_{82}\mathrm{Pb} + {}^{4}_{2}\mathbf{He}$ (α decay)

${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{139}_{53}\mathrm{I} + 3\,{}^{1}_{0}\mathrm{n} + {}^{94}_{39}\mathbf{Y}$ (Nuclear fission)

4. Kinetics of Radioactive Decay

Radioactive decay is a random phenomenon: each decay is an independent event, and it is impossible to predict when a specific nucleus will undergo decay. When a nucleus decays, it is transformed into another nuclide, which can be radioactive or non-radioactive.

The decay of a nuclide is independent of the physical conditions (temperature, pressure, etc.) in which it is found and its chemical state (free or combined in molecules).

4.1. Radioactive Decay Law

The spontaneous decay of nuclide A is represented by the following reaction: A → B
Where B is a formed nuclide and is not radioactive. The kinetics of this reaction is expressed by this equation:

$$-\int_{N_0}^{N_t} \frac{dN}{dt} = \lambda N$$

- N_t: the number of nuclei remaining at time t;
- N_0: the initial number of nuclei.

The separation of variables in the first equation allows us to obtain the following relationship:

$$-\int_{N_0}^{N_t} \frac{dN}{N} = \int_{t=0}^{t} \lambda\, dt$$

The equation obtained after integrating the previous equation is:

$$N_t = N_0\, e^{-\lambda t}$$

Where: λ: The radioactivity constant expressed in s^{-1} or, more generally,

the inverse of the time unit. Nd: The number of nuclei that have decayed,

$$\mathbf{N_d = N_0 - N_t} \;; \qquad \mathbf{N_0 = \frac{m_0}{M} N_A} \;; \qquad \mathbf{N_t = \frac{m_t}{M} N_A}$$

Where:

m_t and m_0: represent the mass at time t and the initial mass, respectively.

N_A: Avogadro's number, which is 6.023×10^{23}.

By analogy, the radioactive decay law can also be expressed in terms of mass using the following equation:

M: the molar mass of a nuclide.

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

4.2. Radioactive Activity

Represents the number of decays per second. The activity at time A(t) is expressed by the following equation:

$$A(t) = -\frac{dN(t)}{dt} = \lambda.\, N_0.e^{-\lambda.t} = A_0 \,.\, e^{-\lambda.t}$$

Where: A_0: represents the initial activity, with: $A_0 = \lambda \,.\, N_0$

The magnitude of activity can be expressed in various units, such as d.p.s (disintegrations per second), Bq (Becquerel), Cu (curie), etc.

Knowing that:

1 d.p.s = 1 Bq

1 Cu = 3.7×10^{10} d.p.s

4.3. The radioactive period or half-life

It is defined as the time required for half of the nuclei present at time t to undergo decay: $\mathbf{N_t = \frac{N_0}{2}}$

As shown in the Figure III.5, the period (T), also known as the half-life (t1/2), is given by the following expression:

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

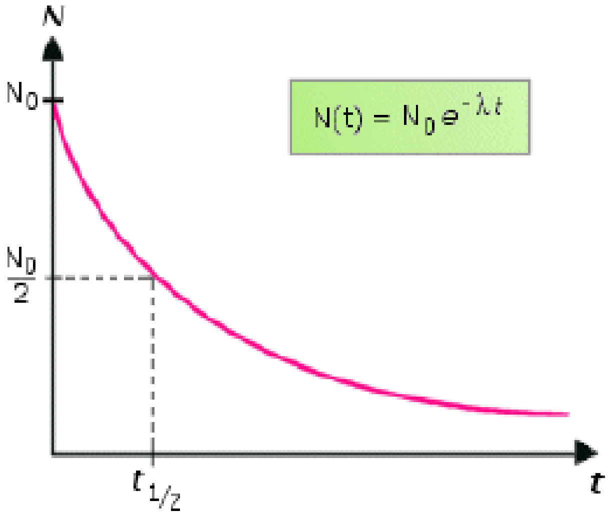


Figure III.5: Decay Kinetics.

Example:

A 10 mg sample of iodine-131 ($^{131}{}_{53}I$) is β^- radioactive. It has a half-life, T, of 8 days.

1-Write the decay equation for iodine 131.

2-Calculate the radioactive decay constant, α, of $^{131}_{53}I$.

3-How much mass of $^{131}_{53}I$.remains after 24 days?

4-Calculate the number of nuclei that remain after 24 days.

5-Deduce the activity after 24 days.

6-Calculate the energy released by the decay of one iodine nucleus in joules and MeV (million electronvolts).

Solution

1-The nuclear equation:

$$^{131}_{53}I \longrightarrow {}^{131}_{54}Xe + {}^{0}_{-1}\mathbf{e} + \upsilon$$

2-The radioactivity constant:

$$\lambda = \frac{\ln 2}{T} = \frac{0.69}{8} = 0.086\ d^{-1}$$

3-The mass of remaining iodine after 24 days:

$m_t = m_0\ e^{-\lambda t} = 10\ .\ e^{-0.086\ x\ 24} = 1.25$ mg

4-The number of remaining nuclei: After one month, which is 30 days:

$N_t = N_0\ e^{-\lambda t} = \frac{m_0}{M}\ N_A\ e^{-\lambda t} = \frac{10}{131}\ 6.023\ 10^{23}\ e^{-0.086\ x\ 24} = 5.7471\ 10^{21}$

Or : $N_t = \frac{m_t}{M} N_A = \frac{1.25}{131} 6.023\ 10^{23} = 5.7471\ 10^{21}$

5-The activity:

$$A(t) = A_0\ e^{-\lambda t} = \lambda\, N_0\ e^{-\lambda t} = \lambda \frac{m_0}{M}\ N_A\ e^{-\lambda t} = 0.086\ \frac{10}{131}\ 6.023\ 10^{23}\ e^{-0.086\ x\ 24}$$

$A(t) = 5.02\ 10^{20}$ dpd

933.75 = - 0.6-The energy released by the decay of one iodine nucleus in joules: Einstein's equation allows us to calculate the energy released during the decay: $\Delta E = \Delta m.c^2$.

$\Delta m = (m_{Xe} + m_e) - m_I = -0.00105$ amu;

$\Delta E = -0.00105 \times 933.75 = -0.980$ Mev;

$\Delta E = -0.980 \times 1.6 \times 10^{-13} = -1.568$ J.

5. Applications of radioactivity

5.1. Tracers for Industrial Manufacturing Processes:

Radioactive isotopes are used as tracers to monitor and control various industrial manufacturing processes, ensuring quality and safety.

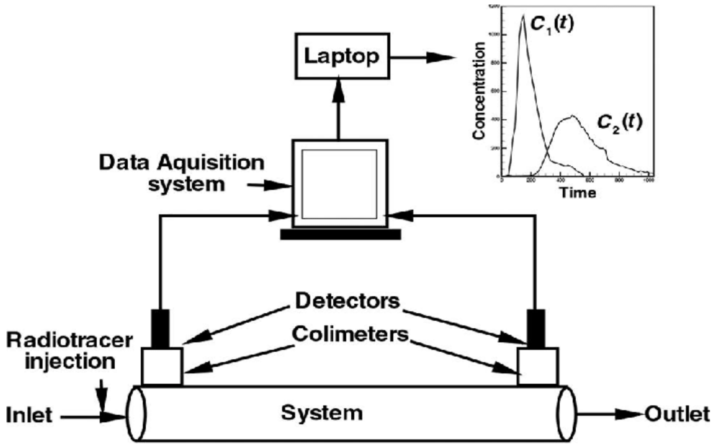


Figure III.6: Uses of radioisotope in industry.

5.2. Energy Source (Electricity Production):

Radioactive materials are used in nuclear power plants to generate electricity through nuclear fission reactions.

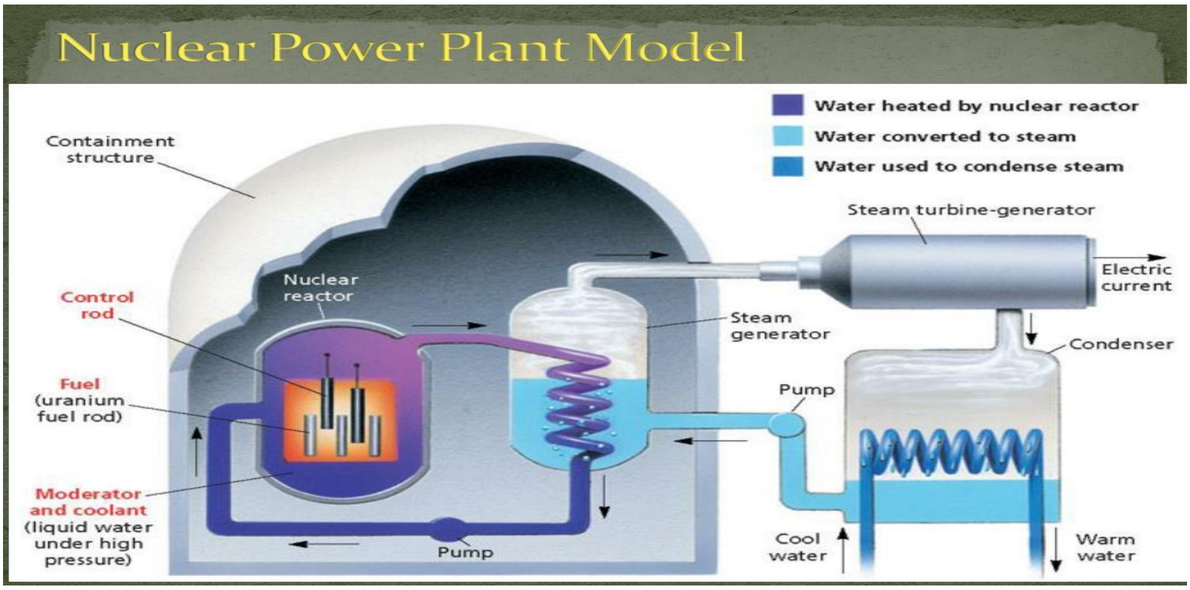


Figure III.7: Nuclear power plant model.

5.3. Medicine:

Radioactive isotopes have numerous medical applications. For example: radioactive iodine is used in thyroid scintigraphy (tracking a radioactive marker in the body) and for treating certain thyroid conditions and tumors.

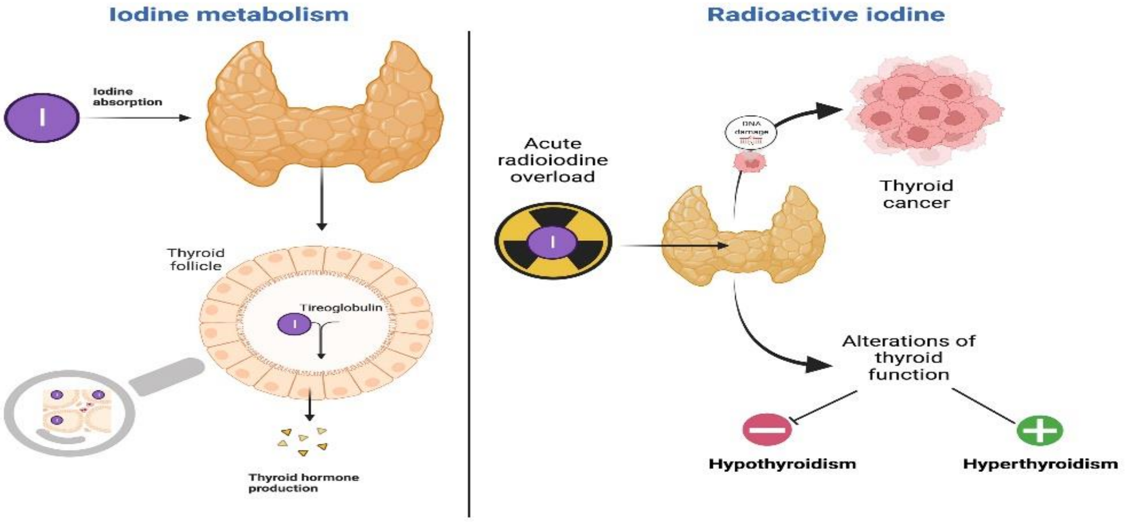


Figure III.8: Iodine 131 Therapy For Thyroid Cancer.

5.4. Archaeological Dating:

Radioactive isotopes, such as carbon-14 (C-14), are used to date ancient samples. C-14 is produced in the atmosphere through cosmic ray bombardment, absorbed by plants as carbon dioxide, and ceases to be absorbed when the plants die. The decay of C-14 over time allows archaeologists to determine the age of organic materials.

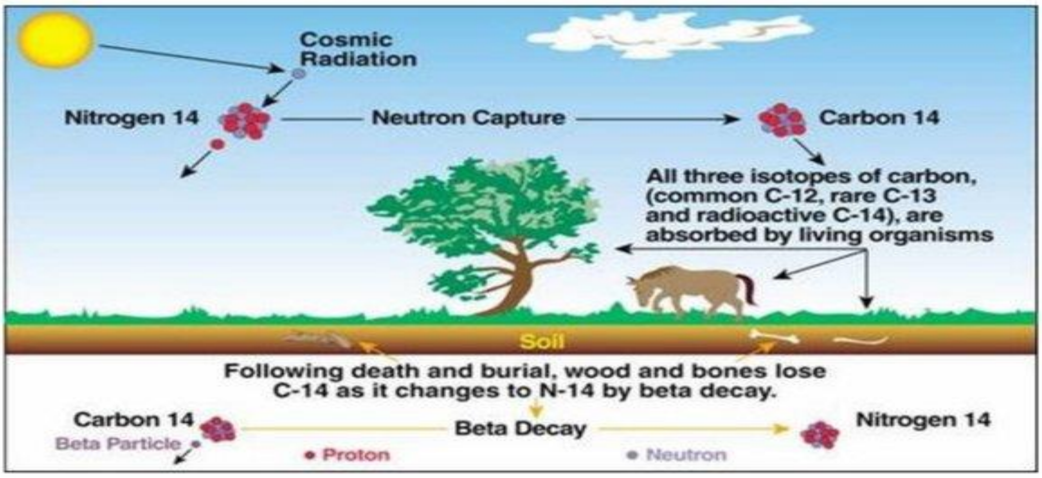


Figure III.9: C-14 carbon dating process.

5.5. Geological Dating:

Various radioactive elements are employed for dating rocks. One example is the use of lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) that result from the decay of uranium and thorium isotopes.

By measuring the ratio of lead atoms to uranium nuclei, the date of the onset of decay in rocks can be calculated.

These applications of radioactivity have significant roles in a wide range of fields, from industry and energy production to healthcare and scientific research.

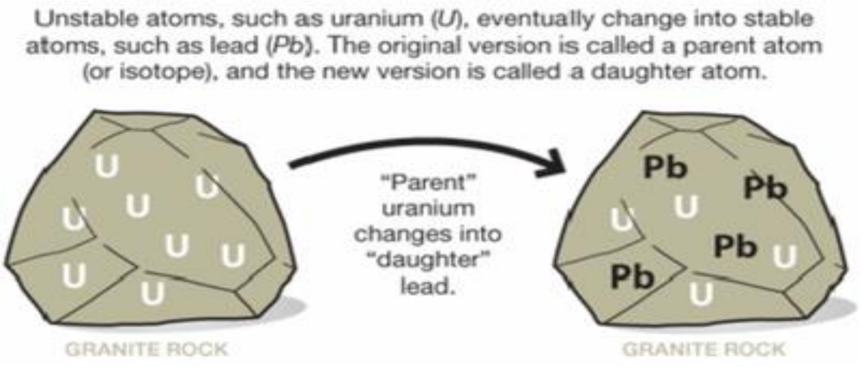


Figure III.10: Radioactive dating.

6. Dangers of radioactivity

6.1. Nuclear Testing and Bombs:

Nuclear weapons and nuclear tests have the potential for catastrophic destruction and long-term environmental contamination.

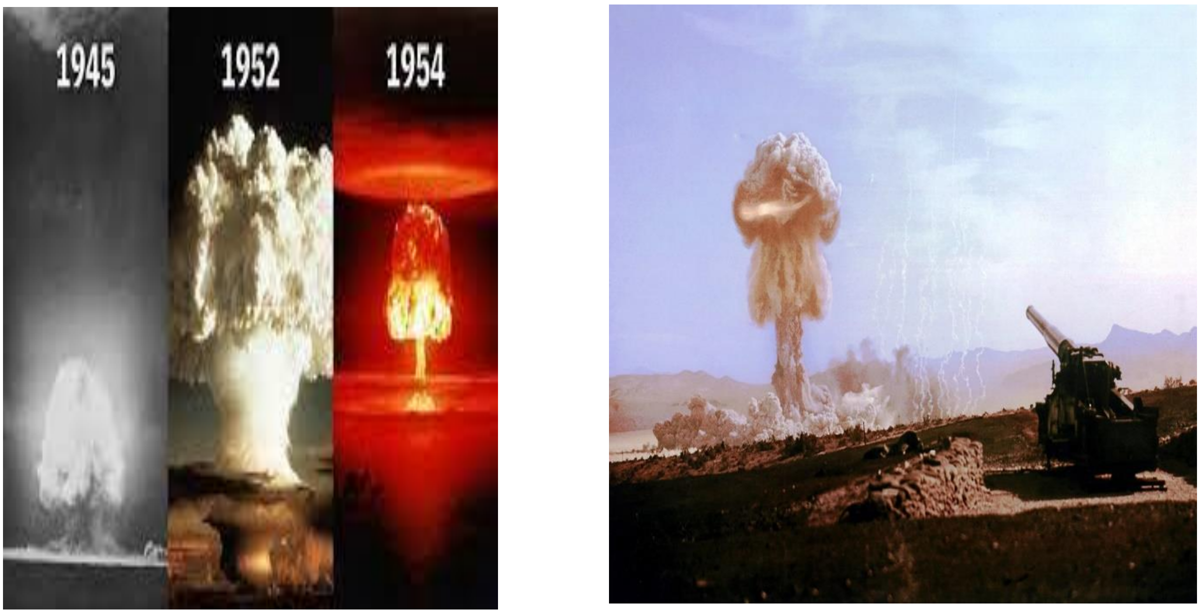


Figure III.11: The Human Cost of Nuclear Testing.

6.2. Waste:

Radioactive waste poses a significant danger due to its long-lasting radioactivity. Proper disposal and containment are crucial to prevent environmental and health hazards.

6.3. Accidents:

Accidents at nuclear facilities, such as reactor meltdowns or radiation leaks, can lead to immediate health risks and long-term environmental contamination.

Figure III.12: Effects of reactor accidents.

7. The effects of nuclear radiation are as follows:

Nuclear radiation is ionizing radiation, meaning it is energetic enough to strip electrons from atoms.

When nuclear particles pass through a substance, like flesh, they collide with electrons and ionize

the atoms they encounter. This can result in the destruction of organic molecules, such as tissue. The effects of ionizing radiation include:

- Pathological Effects: Radiation can cause tissue damage, increase the risk of cancer and leukemia, and lead to various health issues.
- Genetic Effects: Radiation exposure can result in genetic mutations, potentially affecting future generations.

8. Different types of radiation have distinct characteristics:

Alpha (α) Radiation: Alpha particles are relatively low-penetrating and can be stopped by human skin, but they are highly dangerous if ingested.

Beta (β) Radiation: Beta particles are more penetrating, traveling about 1 cm into human tissue, and can be stopped through interactions with atomic nuclei.

Gamma (γ) Radiation: Gamma rays are highly penetrating and can pass through the human body, making them particularly hazardous.

They are capable of causing cancer and other health issues.

All forms of radiation have the potential to induce cancer, and the severity of their effects depends on factors like the type and amount of radiation, the exposure time, and the individual's sensitivity to radiation.

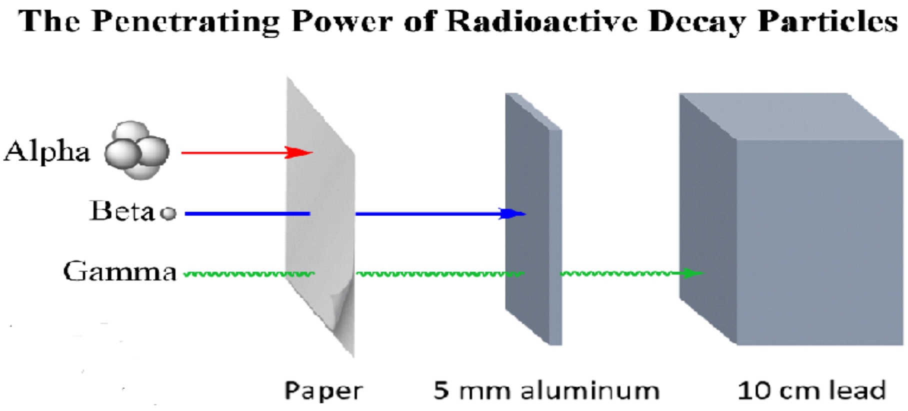


Figure III.13: Types of ionizing radiation.

Corrected Exercises

Exercise 1 Questions 1 and 2 are independent:

1. Complete the following radioactive equations by specifying the type of each reaction.

$^{30}_{15}P \longrightarrow {}^{30}_{14}Si + \ldots\ldots..$

$^{1}_{1}H + \ldots. \longrightarrow {}^{4}_{2}He + \gamma$

$^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + \ldots..$

$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{132}_{51}Sb + \ldots. + 3\ {}^{1}_{0}n$

$^{63}_{29}Cu + {}^{1}_{0}n \longrightarrow {}^{64}_{30}Zn + \ldots\ldots$

$^{14}_{7}N + \ldots\ldots\ldots \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$

$^{9}_{4}Be + {}^{4}_{2}He \longrightarrow \ldots\ldots + {}^{1}_{0}N$

2. An atom X contains in its nucleus 15 protons and 18 neutrons. 1. Since this nucleus is radioactive (emitting β^- particles), write its decay reaction. 2. When it is hit by α particles, the nucleus X transforms into Y with the emission of a neutron. Write the corresponding nuclear reaction.

Exercise 2:

Consider the following two reactions:

$$^{235}_{92}U + {}^{1}_{0}\eta \longrightarrow {}^{93}_{36}Kr + {}^{140}_{56}Ba + \ldots..{}^{1}_{0}n$$

$$^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{A}_{Z}X + {}^{1}_{0}n$$

1. Complete each reaction.

2. Calculate the mass variation and then the energy released during this reaction (in joules and then in MeV).

Data	$^{1}_{0}n$	$^{2}_{1}H$	$^{3}_{1}H$	$^{4}_{2}He$	$^{235}_{92}U$	$^{93}_{36}Kr$	$^{140}_{56}Ba$
Mass (amu)	1,0087	2,0141	3,0165	4,0026	235,0439	93,8946	139,9106

Exercise 3:

A nucleus $^{A}_{Z}X$ reacts with a proton to produce two helium nuclei. What is the nature of X? The reaction is accompanied by a mass decrease Δm. What is the corresponding energy? Is it released or absorbed? Justify your answer.

Data: H = 1,0081 amu; He = 4,0039 amu; Δm = 0,0186 amu; C = 3 10^8 m/s

Exercise 4:

During its spontaneous decay, the atom of radium $^{226}_{88}Ra$ emits an α particle.

a. Write the equation representing this radioactive decay.

b. The mass of the $^{226}_{88}\mathrm{Ra}$ nucleus is 226.096 amu, the mass of the nucleus formed after the decay is 222.0869 amu, and the mass of the α particle is 4.0039 amu. Calculate the energy released by the decay of one radium nucleus.

Exercise 5:

A radioactive substance with a half-life of 10 seconds initially emits 2×10^{7} α particles per second.

1. Calculate the decay constant of the substance.

2. What is the activity of this substance?

3. Initially, how many radioactive nuclei are there?

4. How many radioactive nuclei will remain after 30 seconds? What will the activity of the substance be at that time?

Exercise 6:

The $^{45}_{20}\mathrm{Ca}$ has a half-life T of 163 days. Calculate the value of the radioactive constant λ in day^{-1} and s^{-1}. Calculate the percentage of nuclei that remain after 90 days.

Exercise 7:

Calculate the mass corresponding to an activity of 1 Ci (curie) for each of the following radionuclides: $^{131}_{53}\mathrm{I}$, $^{226}_{88}\mathrm{Ra}$, $^{238}_{92}\mathrm{U}$

Data: Half-life of $^{131}_{53}\mathrm{I}$: T=8 days; $^{226}_{88}\mathrm{Ra}$ T: =1620 years; $^{238}_{92}\mathrm{U}$: T = 4.5 billion years.

1 Ci = 3.7×10^{10} Becquerel (Bq).

Exercise 8:

The activity of a sample of organic material from an archaeological piece is A=1180 dps, and the activity of the same quantity of current organic material is $A0$=1980. Determine the age of this archaeological piece.

Data: Half-life of carbon-14: T=5590 years.

Exercise 9:

The isotope $^{40}_{19}K$ has a half-life of T 1.3×10^{9} years and constitutes 0.012% of the potassium found in nature. Potassium in the human body represents approximately 0.35% of body weight. Calculate the total radioactivity (expressed in DPM, Ci, and Bq) resulting from the decay of potassium-40 in a 75 kg individual.

Exercise 10:

Calculate the activity of 10 µg of sodium iodide (INa), knowing that 20% of the iodine atoms are radioactive $^{131}_{53}\mathrm{I}$ and 80% are stable $^{127}_{53}\mathrm{I}$.

What is the rate of β^-radiation emission?

Data: Data: Half-life of ${}^{131}_{53}\mathrm{I}$: T=8 days; Molar mass of Na = 23; Avogadro's number $N_A=6.023\times10^{23}$; $I\beta=89.9\%$.

Correction

Exercise 1:

1. Complete the following radioactive equations by specifying the type of each reaction.

${}^{30}_{15}\mathrm{P} \longrightarrow {}^{30}_{14}\mathrm{Si} + \mathbf{{}^{0}_{+1}e}$ Emission of β+

${}^{1}_{1}\mathrm{H} + \mathbf{{}^{3}_{1}H} \longrightarrow {}^{4}_{2}\mathrm{He} + \gamma$ Emission of γ

${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + \mathbf{{}^{1}_{0}n}$ Nuclear fusion

${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{132}_{51}\mathrm{Sb} + \mathbf{{}^{101}_{41}X} + 3\ {}^{1}_{0}\mathrm{n}$ (X= Nb) Nuclear fission

${}^{63}_{29}\mathrm{Cu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{64}_{30}\mathrm{Zn} + \mathbf{{}^{0}_{-1}e}$ Emission of β^-

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

${}^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow \mathbf{{}^{12}_{6}X} + {}^{1}_{0}\mathrm{N}$ (X=C) Transmutation (α,n)

2. The nuclear reaction

${}^{33}_{15}\mathrm{X} \longrightarrow {}^{33}_{16}\mathrm{Y} + {}^{0}_{-1}\mathrm{e}$ Emission of β^-

${}^{33}_{15}\mathrm{X} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{36}_{17}\mathrm{A} + {}^{1}_{0}\mathrm{n}$ Transmutation (α,n)

Exercise 2:

1. The nuclear reaction

$$ {}^{235}_{92}\mathrm{U} + {}^{1}{}_{0}\eta \longrightarrow {}^{93}_{36}\mathrm{Kr} + {}^{140}_{56}\mathrm{Ba} + \mathbf{3}\ {}^{1}_{0}\mathrm{n} $$

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow \mathbf{{}^{4}_{2}He} + {}^{1}_{0}\mathrm{n} $$

2. **The mass variation and the energy released**

$\Delta m = (m^{93}\mathrm{Kr} + m^{140}\mathrm{Ba} + 3m_n) - (m^{235}\mathrm{U} + m_n) = 93.8946+139.9106+ 3\mathrm{x}1.0087-235.0439-1.0087$

$\Delta m = 0.7787\mathrm{amu} = 0.7787 \times 1.66 \times 10^{-27} = 1{,}2926\ 10^{-27}$ kg

$\Delta E = \Delta m\, C^2 = 1{,}2926\ 10^{-27}\,(3 \times 10^8)^2 = 11.6337\ 10^{-11}$ Joule.

$\Delta E = 11.6337\ 10^{-11}$ Joule $= \frac{11.6337\ 10^{-11}}{1.6\ 10^{-19}}$ eV $= 7.2711\ 10^8$ eV= 727.11 MeV.

Or 1 amu gives 933.75 MeV: $\Delta E = 0.7787\mathrm{amu} \times 933.75 = 727.11$ MeV.

The same applies to the second reaction.

Exercise 3:

a. **The nature of** $\boldsymbol{X}$

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

The element X is lithium: $^{7}_{3}Li$

b. The corresponding energy

$\Delta E = \Delta m.C^2 = 0{,}0186 \text{ x } 1{,}66\ 10^{-27} \text{ x } (3\ 10^{8})^2 = 2.778\times10^{-12}$ joules.

Since Δm=0.0186 amu is positive, the energy is also positive. Therefore, this energy is absorbed.

Exercise 4:

a. The nuclear reaction

$^{226}_{88}\text{Ra} \xrightarrow{\qquad} ^{222}_{86}\text{X} + ^{4}_{2}\text{He}$ (X=Rn) Emission of α

b. The energy released

$\Delta m = m_{Rn} + m_{He} - m_{Ra}$

$\Delta m = 222.0869 + 4.0039 - 226.096 = -0{,}0052$ amu.

$\Delta E = -0{,}0052 \text{ x } 933 = -4{,}6$ Mev.

Exercise 5 :

1. The decay constant of the substance

$$\lambda = \frac{\ln 2}{T} = \frac{\ln 2}{10} = 0{,}0693\ s^{-1}$$

2. The activity of this substance:

$A_0 = 2.\ 10^{7}$ Bq (1 alpha particle emitted corresponds to 1 nucleus of the substance disintegrated)

3. The initial number of radioactive nuclei

$N_0 = A_0 / \lambda = 2.\ 10^{7}/0{,}0693 = 2{,}89.\ 10^{8}$ Nuclei.

4. The number of radioactive nuclei after 30 s

After 30 s, that is to say 3 half-lives, there will remain:

$N_t = N_0\ e^{-\lambda t} = 2{,}89.\ 108\ e^{-0{,}069 \text{ x } 30} = 3{,}6.\ 10^{7}$ Nuclei.

5. The activity of the substance

$A_t = \lambda.\ N_t = 2{,}5.\ 10^{6}$ Bq = 2,5 kBq.

Exercise 6:

1. Calculation of the radioactive constant:

$$\lambda = \frac{\ln 2}{T} = \frac{\ln 2}{163} = 4{,}25\ 10^{-3}\ \text{day}^{-1}$$

$$\lambda = \frac{\ln 2}{T} = \frac{\ln 2}{163\ x\ 8.64\ 10^{4}} = 4{,}92\ 10^{-8}\ \text{s}^{-1}$$

2. The percentage of nuclei after 90 days:

The integrated radioactive decay law is written as:

$N_t = N_0 . e^{-\lambda t}$ with: N_0 = 100% = 1

$N_t = 1\ e^{-4{,}25\ 10^{-3}\ x\ 90} = 0{,}682 = 68{,}2\ \%$

Exercise 7:

$A_t = N_t . \lambda$……….(1)

$N_t = \frac{m_t}{M} N_A$……..(2)

We substitute (2) into (1):

$A_t = \frac{m_t}{M} N_A . \lambda$ $\qquad \lambda = \frac{\ln 2}{T}$

$A_t = \frac{m_t}{M} N_A . \frac{\ln 2}{T}$

So: $m_t = \frac{At.\ M.T}{N_A \ln 2} = \frac{At.\ M.T}{6.023\ 10^{23}\ .0.693} = 0.24\ .\ 10^{-23}\ A_t\ .\ M\ .\ T$

A is the activity in Becquerels (1 Ci = 3.7×10^{10} Bq);

N_A is Avogadro's number 6.023×10^{23} ;

λ is the decay constant;

N_t is the number of radioactive nuclei.

T is the half-life of the radionuclide.

M is the Molar mass.

$^{131}_{53}$I : m = 0,24 10^{-23} x 131 x 3,7 10^{10} x (8 x 8,64 10^{4}) = 8 10^{-6} g = 8 µg.

$^{226}_{88}$Ra : m = 0,24 10^{-23} x 226 x 3,7 10^{10} x (1620 x 365 x 8,64 10^{4}) = 1,02 g.

$^{238}_{92}$U : m = 0,24 10^{-23} x 238 x 3,7 10^{10} x (4,5 10^{9} x 365 x 8,64 104) = 3106 g.

Exercise 8 :

$A_t = \lambda N_0 e^{-\lambda t}$ $\qquad A_0 = \lambda N_0$ and $\lambda = \frac{\ln 2}{T}$

So: $A_t = A_0\ e^{\frac{-ln2}{T}t}$ $\qquad \frac{A_t}{A_0} = e^{\frac{-\,ln2}{T}t}$

$$ln\,\frac{A_t}{A_0} = -\,\frac{ln2}{T}\,t$$

$$ln\,\frac{A_0}{A_t} = \frac{ln2}{T}\,t$$

$t = ln\,\frac{A_0}{A_t}\,\frac{T}{ln2} = ln\,\frac{1980}{1180}\,\frac{5590}{0.693} = 4175$ years

Exercise 9:

Total potassium mass in the body: $m_K = 0.0035\times m_{body} = 0.0035\times 75 = 0.2625$ kg = 262.5 g.

Mass of ^{40}K in the body: $\mathbf{m_{40K}} = 1.2\times 10^{-4}\times 262.5 = 0.0315$ g.

Convert the mass of ^{40}K to moles:

$n_{40_K} = \frac{m_{40K}}{M_K} = \frac{0.0315}{40} = 7.87\ 10^{-4}$mol.

Number of $_{40}$K atoms: $N_{40K}=n_{40K}\times N_A = (7.87\ 10^{-4})\times(6.023\times 10^{23}) = 4{,}74\ 10^{20}$ atoms.

Decay constant (λ): $\lambda=\ln(2)/T = Ln\ 2 / T = 0{,}693 / (1{,}3\ 10^9 \times 365 \times 24 \times 60) = 1{,}014\ 10^{-15}\ min^{-1}$.

Activity (A) in DPM: $A=\lambda\times N_{40K} = (1{,}014\ 10^{-15} \times 4{,}74\ 10^{20}) = 4{,}81\ 10^5$ DPM.

Activity (A) in Ci= $(4{,}81\ 10^5 / 2{,}22\ 10^{12}) = 0{,}217\ 10^{-6}$ Ci.

Activity (A) in Bq = $(0{,}217\ 10^{-6} \times 3{,}7\ 10^{10}) = 8029$ Bq.

Exercise 10:

Calculation of the average molar mass of the two types of $^{131}_{53}$I and $^{127}_{53}$I molecules:

M = [(131 x 0,2) + (127 x 0,8)] + 23 = 150,8 g/mol,

Calculate the number of moles of Ina:

$n_{INa}= \frac{m_{INa}}{M_{INa}} = \frac{10\ 10^{-6}}{150.8} = 6.63\times 10^{-8}$mol.

Calculate the total number of iodine atoms:

Each molecule of INa contains one atom of iodine. Therefore, the total number of iodine atoms is:
$NI=n_{INa}\times N_A=(6.63\times 10^{-8})\times(6.023\times 10^{23})= 3.99\times 10^{16}$ atoms.

Calculate the number of radioactive iodine-131 atoms:

The fraction of iodine-131 is =0.2. Thus, the number of radioactive iodine atoms is:
$N_{131I} = 0.2\times 3.99\times 10^{16} = 7.98\times 10^{15}$atoms radioactive iodine.

Calculate the activity (A):

$A = (Ln\ 2\ .\ N_{131I})/ T = (0{,}693 \times 7{,}98\ 10^{15}) / (8 \times 8{,}64\ 10^4) = 8\ 10^9$ Bq

$A = (8.10^9 \times 3{,}7\ 10^{10}) = 0{,}22$ Ci

Rate of β-radiation emission:

The rate of β^-radiation emission is determined by the fraction of β^-decays:

Rate of β-emission=$I\beta^- \times A = 8.10^9$ x 0,899 = 7,2 10^9 Bq.

Chapter IV:
Electronic Structure of the Atom

1. Introduction

The theory of atomic electron structure is based on the laws describing the movement of electrons. To reconcile the dual nature of electrons, which are both particles with mass (as demonstrated by the experiments of Millikan and Thomson) and waves, various experiments have been conducted, and multiple theories have been proposed.

2.Wave Theory of Light

2.1. Light Waves

It is accepted that light is an association of electric and magnetic fields that propagate through space with a wave motion.

These electromagnetic or light waves propagate through space at a constant speed C (the speed of light), equal to 3×10^8 m/s. Each of these waves is characterized by its wavelength $\lambda = C.T$ or its wave number $\bar{\upsilon} = 1/\lambda$.

The period T is the time it takes for the vibrating vector ($\vec{E}$ et $\vec{B}$) to return to the same magnitude and in the same direction.

The number of wavelengths traveled per second, known as the frequency ν of light, is given by:

$$\upsilon = \frac{C}{\lambda} = \frac{1}{T}$$

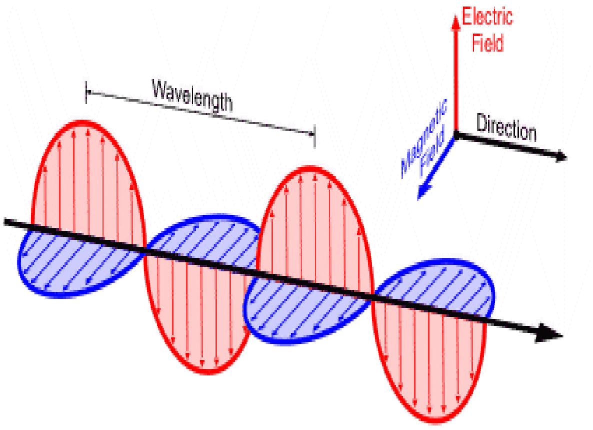


Figure IV.1: Diagram of an electromagnetic or light wave.

The electromagnetic spectrum consists of all light waves where the frequency ν can take on a continuous range of values. The visible spectrum is only a small portion of the complete electromagnetic radiation spectrum (Figure IV.2). It represents the part of the full spectrum to which the human eye is sensitive. It extends from violet to red.

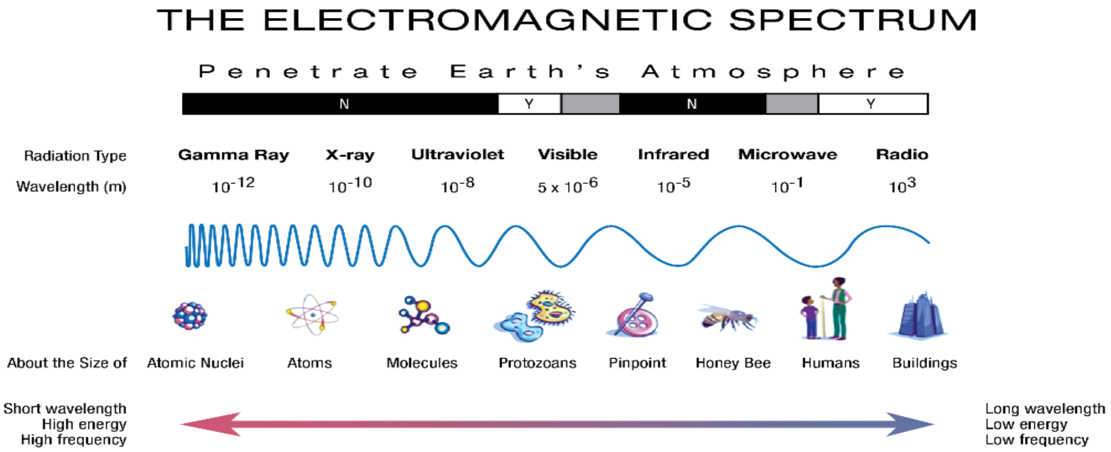


Figure IV.2: Electromagnetic Spectrum.

2.2. Quantum Theory (Corpuscular Nature of Light)

Each component of white light is a luminous radiation characterized by a specific color (composed of an infinity of colors: red, blue, violet, etc.), and each color corresponds to a specific energy, frequency, and wavelength.

Planck's studies led to the conclusion that a light ray is made up of infinitely small energy packets called photons, with each photon carrying an energy ΔE:

$$\Delta E = h.\upsilon = h.\frac{c}{\lambda}$$

With h being the Planck constant: $h = 6.62 \times 10^{-34}$ J·s.

E: Energy of the light carried by the radiation in joules, ν: Frequency of the radiation in s^{-1} (or Hz).

2.3. The photoelectric effect

The photoelectric effect was discovered by Hertz around 1885.

A monochromatic light with increasing frequency ν irradiates a metal plate connected to a discharged dial electrometer at the initial moment.

The electrometer begins to charge beyond a certain frequency.

The two branches of the electrometer separate, indicating the presence of electricity.

When a metal plate is illuminated, and a frequency scan is performed on the light, electron emission is obtained from a threshold frequency ν_0 that is characteristic of the metal used.

According to Einstein, light carries grains of matter, the "quanta," also called "photons," each carrying an energy $\Delta E = h \cdot \nu$.

These energy grains strike the metal atoms of the plate, and if they have enough energy, they remove electrons from the plate, resulting in the production of electricity.

This is what constitutes the "photoelectric effect."

So, when the surface of a metal is irradiated with light of a given frequency, electrons are emitted (removed).

Electron emission only occurs if the frequency of the incident light is greater than a specific threshold value ν_0 for each metal.

The kinetic energy ($mv^2/2$) of the ejected electron increases as the frequency ν of the light increases.

Experiment:

If a metal plate is illuminated with monochromatic light of frequency ν greater than the threshold frequency ν_0, the excess energy compared to the

characteristic energy of the metal $E_0 = h\nu_0$ is dissipated in the form of kinetic energy taken by the electrons.

$E_C = E - E_0 = h\nu - h\nu_0 = h\,(\boldsymbol{\nu - \nu_0})$

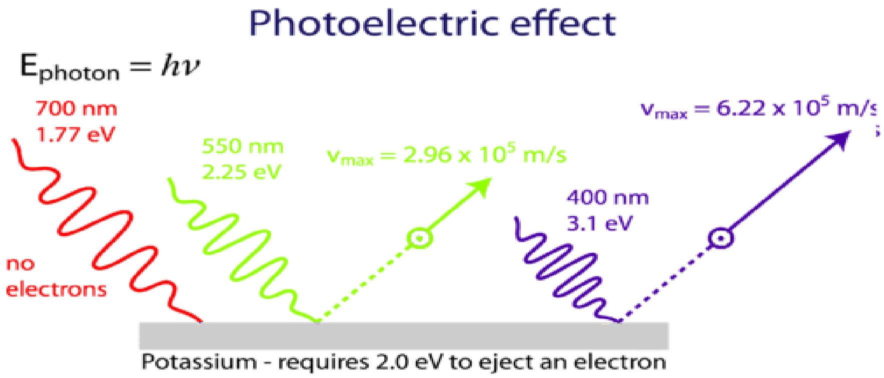


Figure IV.3: Photoelectric effect.

Note:

1. Only light with a frequency $\nu \geq \nu_0$ determines electron emission.
2. If a photon with energy $(E = h\nu) \geq (E_0 = h\nu_0)$ is absorbed, the emitted electron will reach a maximum kinetic energy:

$$\mathbf{E_C = 1/2\ mv^2 = h\ (\nu - \nu_0)}$$

Exercise of application:

A polychromatic light consisting of 3 radiations (λ_1 = 450nm; λ_2 = 610nm; λ_3 = 750nm) irradiates a sample of potassium contained in a bulb. The ionization energy is 2.14 eV (the energy required to remove an electron from a potassium atom).

1. Establish the relationship $E\ (eV) = 1241/\lambda\ (nm)$.
2. Which radiations lead to the photoelectric effect?
3. What is the speed of the electrons expelled from the metal? Electron mass 9.1×10^{-31} kg.

Solution:

Photon energy $E = h\nu = hc/\lambda$, $E(J) = 6.62 \times 10^{-34} \times 3 \times 10^{8} / \lambda$.

$1\ eV = 1.6 \times 10^{-19}$ J, and $1\ nm = 10^{-9}$ nm. $E\ (eV) = 1241/\lambda$ (nm).

Use the above relationship to calculate the energy for each photon:

$E_1 = 1241/450 = 2.76$ eV;

$E_2 = 2.03$ eV;

$E_3 = 1.65$ eV. Only the radiation λ_1 is sufficiently energetic.

The electron removed from the atom carries away 2.76 - 2.14 = 0.62 eV as kinetic energy.

$\frac{1}{2} mv^2 = 0.62 \times 1.6 \times 10^{-19} = 10^{-19}$ J; $v^2 = 10^{-19} / (0.5 \times 9.1 \times 10^{-31})$.

Therefore, $v \approx 4.7 \times 10^{5}$ m/s.

3. Interaction between light and matter

When a source of light energy strikes an object, that object will emit radiation at a specific wavelength and therefore appear as a particular color, depending on processes of emission, reflection, absorption, and transmission.

3.1. Emission spectrum of the hydrogen atom

This is the simplest atomic emission spectrum, obtained when dihydrogen H_2 is subjected to a very low pressure (≈1 mmHg) electrical discharge created by a high-voltage generator. This discharge dissociates the H-H bond in the dihydrogen molecule, thus exciting hydrogen atoms. The excited atoms have energy that they release as they return to lower energy states by emitting electromagnetic radiation at different wavelengths.

A prism is used to analyze the emitted light, resulting in several groups of bright lines on a dark background on a photographic plate.

The collection of bright lines constitutes the emission spectrum of hydrogen.

The experiment has shown that this emission spectrum has a large number of lines in the ultraviolet, visible, and infrared regions. Each group of lines is called a series and is named after the scientist who discovered it.

The first lines studied are in the visible range and belong to the "Balmer series."

3.2. Visible line spectrum of the hydrogen atom

3.2.1. Empirical Balmer-Rydberg relation

The analysis of the electromagnetic radiation emitted by excited hydrogen atoms shows that it consists of four distinct visible lines: red (R), blue (B), indigo (I), and violet (V), respectively called H_α, H_β, H_γ, and H_δ.

This is the visible line spectrum of the hydrogen atom.

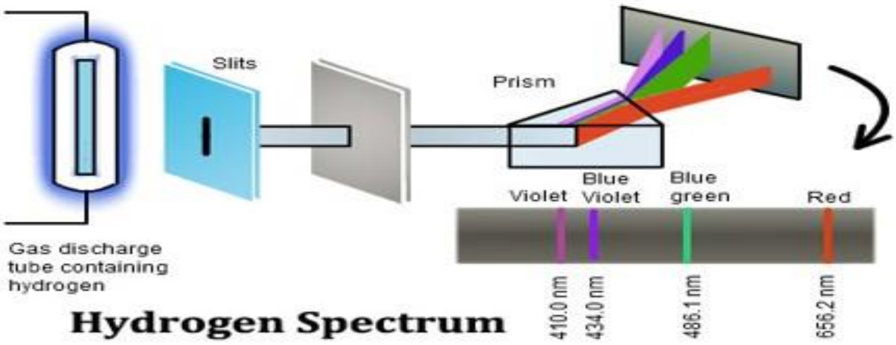


Figure IV.4: Emission spectrum of the hydrogen atom.

Balmer proposed an empirical formula in 1885 to calculate the wavelengths (λ) of the visible hydrogen lines (Balmer series). His formula was later generalized by Rydberg, who expressed it in terms of wavenumber ($\bar{\nu}$), not frequency.

$$\lambda = b(\frac{n_2^2}{n_2^2 - 4}) \; with \; n_2 = 3,4,5, \ldots$$

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

λ: is the wavelength.

$\bar{\nu}$ is the wavenumber (cm^{-1}),

n: integer, $n_1 = 2$ and $n_2 = 3, 4, 5, \ldots$

$R_H = 1.097 \times 10^5 \ cm^{-1}$: Rydberg constant for the hydrogen atom determined experimentally. For n = 3, 4, 5, 6, the frequencies of the four lines can be found.

3.2.2. Concept of Line Series

Ritz generalized the Balmer-Rydberg formula to all the lines of the hydrogen atomic emission spectrum. These lines are grouped into spectral series, located in various wavelength ranges.

Each series is distinguished by the name of the scientist who discovered it and corresponds to the electron's relaxation to an energy level.

For example, the first series, known as the **Lyman** series, corresponds to the electron returning from an excited state to the ground state (n_1=1 and n' > n).

The hydrogen atom's emission spectrum is composed of monochromatic radiations with well-defined wavelengths.

Experimental observations have shown that the hydrogen atom's emission spectrum contains numerous lines in the ultraviolet, visible, and infrared regions. The first lines studied are found in the visible range and belong to the "**Balmer series**".

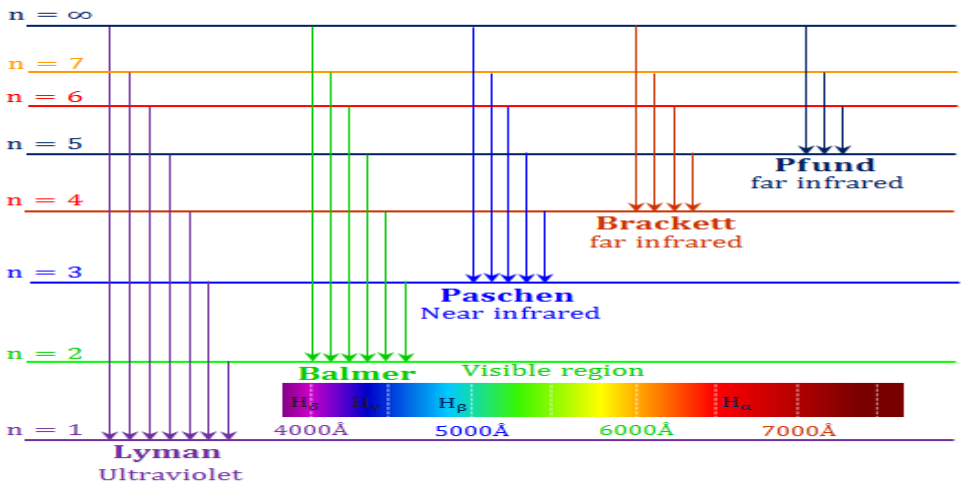


Figure IV.5: Series of Lines in the Hydrogen Atom's Spectrum.

3.2.3. Interpretation of the Hydrogen Emission Spectrum

Due to the high voltage, the electron in H_2 is excited, absorbing energy and moving away from the nucleus, making it unstable. To regain stability, it prefers to return near the nucleus, emitting energy in the form of visible light radiation (photons with frequency ν).

Absorption of Light: When the hydrogen atom is not excited, the electron is in a low-energy orbit, which is called the ground state. When this atom is subjected to a potential, it absorbs energy, resulting in an electronic transition from the ground state to a higher energy level (excited state).

Emission of Light: The excited electron in the atom is in an unstable state and returns to its most stable energy level, the ground state, emitting radiation. The hydrogen emission spectrum shows that only certain energy levels are allowed.

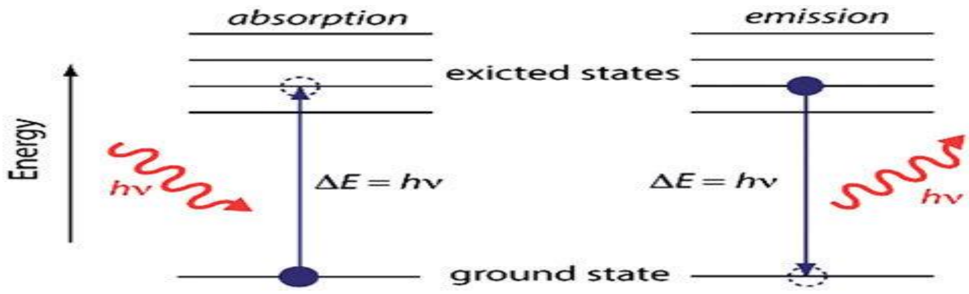


Figure IV.6: Diagram of an Electronic Transition.

Exercise of application:

The element Strontium is known for producing a bright red color in flames. This color is due to the presence of two visible lines in its spectrum, at 605 nm and 461 nm. One of these lines appears yellow-orange, and the other is blue.

1. Assign the color to each of these lines.
2. Calculate the energy and frequency of the corresponding photons.

Solution:

The visible spectrum extends approximately from 400 nm to 800 nm. The order of colors is well-known as ROYGBIV: Red - Orange - Yellow - Green - Blue - Indigo - Violet.

Violet corresponds to high energy, high frequency, and short wavelengths.

Conversely, red corresponds to low energy, low frequency, and long wavelengths. It is easy to assign a color to each line based on this information.

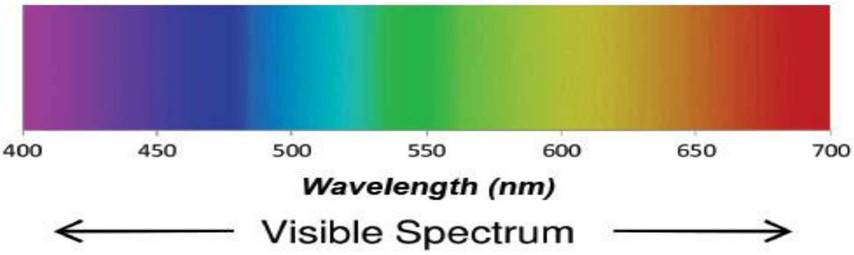


Figure IV.7: The electromagnetic spectrum.

$\upsilon = c / \lambda$

$E = h\upsilon = h\ c / \lambda$

Line 1 : $\lambda_1 = 605$ nm

$\upsilon_1 = 3.\ 108 / 605\ .10^{-9} = 4{,}96.10^{14}$ Hz

$E_1 = 6{,}62.10^{-34} \times 4{,}96.10^{14} = 3{,}28.10^{-19}$ J

Color: Yellow-orange (long wavelength, low frequency, and low energy)

Line 2 : $\lambda_2 = 461$ nm

$\upsilon_2 = 3.\ 10^{8} / 461.10^{-9} = 6{,}51.10^{14}$ Hz

$E_2 = 6{,}62.10^{-34} \times 6{,}51.10^{14} = 4{,}31.10^{-19}$ J

Color: Blue (short wavelength, high frequency, and high energy)

4.Bohr Model

4.1. Description (Hydrogen Atom Case)

To resolve the previous contradictions, Bohr proposed four hypotheses:

- In the atom, the nucleus is stationary, while the electron with mass m moves around the nucleus in a circular orbit with radius r.

- The electron can only be in specific orbits without emitting energy; these are called "stationary orbits."
- When an electron moves from one level to another, it emits or absorbs energy: ΔE = hν
- The angular momentum of the electron can only take on certain values (quantization of angular momentum): mvr = n.h/2π

Where h is the Planck constant and n is a natural number.

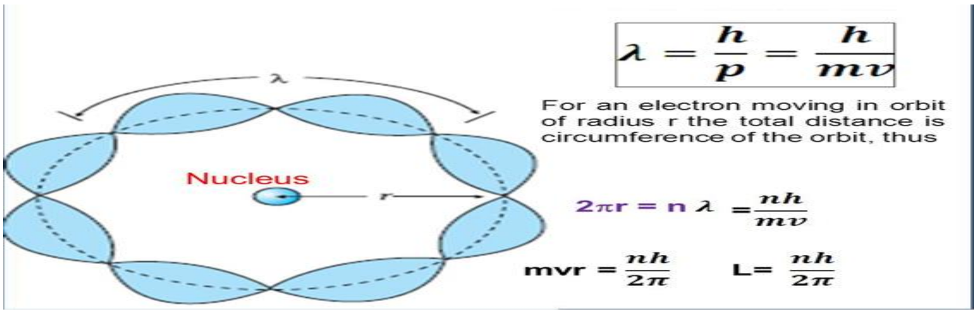


Figure IV.8: The angular momentum of an electron.

4.2. Quantitative Aspect of the Bohr Atom

The system is stable due to the two forces: electrostatic attraction:

$$\overrightarrow{|F_a|} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

Where:

- e is the elementary charge of the electron, with a value of 1.602×10^{-19},
- r is the distance between the electron and the nucleus (i.e., the radius of the electron's orbit),
- ε_0 is the vacuum permittivity (electric constant), with a value of 8.854×10^{-12} F/m.

This expression represents the Coulomb force exerted by the positively charged nucleus on the negatively charged electron, assuming a classical circular orbit as in the Bohr model. The force is directed toward the nucleus and balances the centrifugal force due to the electron's circular motion.

centrifugal force:

$$\overrightarrow{|F_a|} = \frac{m\,v^2}{r^2}$$

Where :

- m is the mass of the electron (9.109×10^{-31}),
- v is the linear speed of the electron,
- r is the radius of the orbit.

The system is in equilibrium if:

$$\overrightarrow{|F_a|} = \overrightarrow{|F_c|} \qquad\qquad m\,v^2 = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

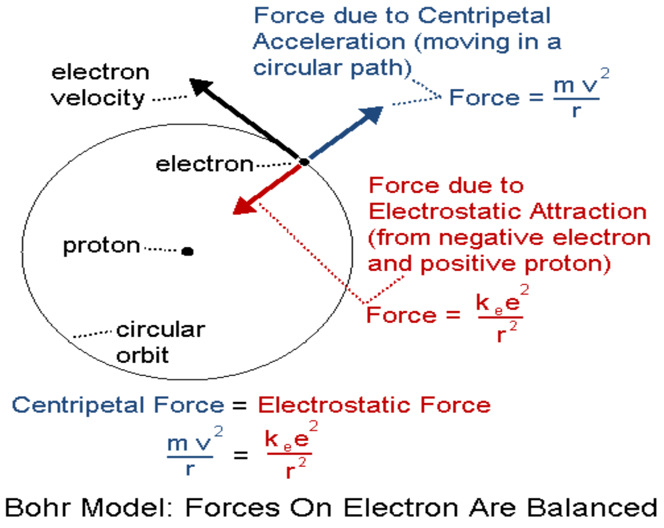


Figure IV.9: Wave nature of electron.

4.2.1. Orbit Radius

We know that: $mvr = n\hbar/2\pi$ So, $mv^2 = n^2\hbar^2 / 4\pi^2 mr^2$

4.2.2. Total Energy of the System

$E_T = E_c + E_p$

E_c: kinetic energy ($E_c = mv^2/2$) and E_p: potential energy, it is due to the nucleus's attraction ($E_p = -e^2/4\pi\varepsilon_0 r$)

$$E_T = \frac{-\,e^2}{8\pi\varepsilon_0 r}$$

Where:

e: is the charge of the electron.

r: is the distance between the electron and the nucleus.

ε_0**:** is the permittivity of free space, which affects the intensity of the interaction between the charge of the electron and that of the proton.

$r = \varepsilon_0 h^2 n^2 / \pi m e^2$

Is the orbit of the electron where it circulates; it is quantized: $E_T = -me^4 / 8\varepsilon_0^2 h^2 n^2$

The total energy of an electron is therefore discrete or quantized.

For n=1 (ground state: the electron occupies the orbit with a radius of r_1 and an energy of E_1):

$r_1 = 5{,}29.10^{-11}$ m = 0,529 Å (1Å = 10^{-10} m)

E_1 = -21,78.10^{-19} J = -13,6 eV (1eV = 1,6.10^{-19}J)

For n = 2 (first excited state), $r_2 = 4r_1$ = 2,116 Å et $E_2 = E_1/4$ = -3,4 eV

For n = 3 (second excited state), $r_3 = 9r_1$ = 4,761 Å et E_3 = -1,51 eV.

The most important equation stemming from Bohr's model expresses the energy levels of the electron in the hydrogen atom:

$E_n = -\ 2{,}178.10^{-18}(Z^2/n^2)$ (J) $E_n = -\ 13{,}6\ (Z^2/n^2)$ (eV)

Where:

n is an integer (higher n values correspond to larger orbit radii).

Z is the effective charge of the nucleus.

The negative sign simply indicates that the electron's energy is lower near the nucleus than at an infinite distance (n = ∞), where, in the absence of any interaction, the energy is zero.

In multi-electron atoms, the energy of an electron can be approximated using a modified version of the Bohr model, taking into account the effective charge Zeff felt by the electron. The general energy formula is influenced by the distance of the electron from the nucleus (radius), the electron mass, the electron charge, and the effective charge of the nucleus.

$$r_n = \frac{n^2\ \varepsilon_0\ h^2}{\pi m_e e^2 Z_{eff}}$$

$$E = -\frac{Z_{eff}^2\ e^2}{8\ \pi\varepsilon_0 r}$$

$$E = -\frac{m\ Z_{eff}^2\ e^4}{2\varepsilon_0\ h^2 n^2}$$

4.3. Absorption and Emission of Energy

An electron can only absorb or emit energy, i.e., radiate, when transitioning from one level (orbit) to another. The amount of energy absorbed or emitted is equal to the difference in energy between the two levels (Planck's relation).

$\mathbf{\Delta E = E_f - E_i}$

Where:

E_f: Energy of the final state.

E_i: Energy of the initial state.

4.3.1. Absorption

When an electron moves from a level n with a radius rn to an orbit n+1 with a radius rn+1, it absorbs radiation of frequency νn+1→n.

4.3.2. Emission

When an electron transitions from a level n+1 to a level n, it emits radiation with a frequency $\nu n+1 \rightarrow n$.

These transitions and energy levels can be represented on an energy level diagram.

For hydrogen (H), you can observe all the series of spectral lines resulting from photons emitted during possible transitions. These series include the Lyman series (n_f=1), Balmer series (n_f=2), Paschen series (n_f=3), Brackett series (n_f=4), and Pfund series (n_f=5) (Figure IV.10).

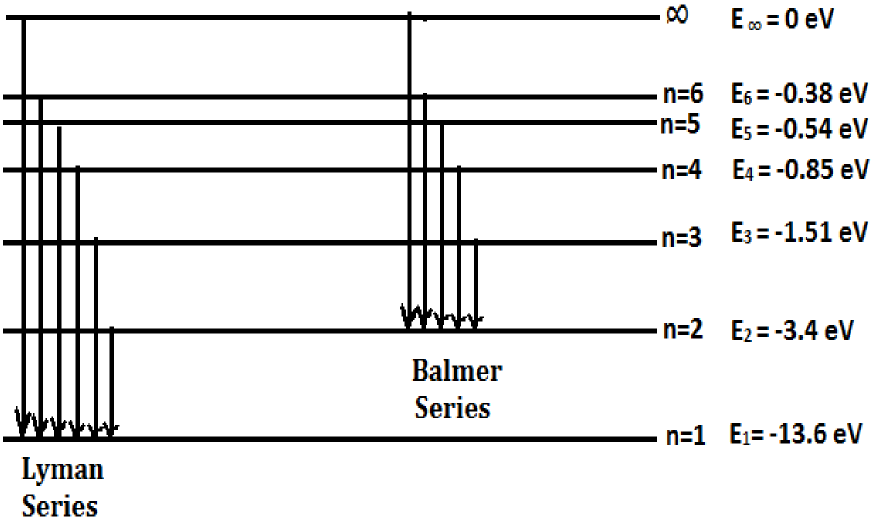


Figure IV.10: Energy Levels of the Hydrogen Atom.

Exercise of Application

What is the wavelength emitted when an electron transitions from the initial level ni = 3 to the final level nf = 2?

Solution :

$E_n = - 13,6 (Z^2 /n^2)$

$E_2 = -3,40$ eV et $E_3 = -1,51$ eV

$\Delta E = E_2 – E_3$

$\Delta E = - 1,89$ eV

Conversion to Joules: $\Delta E = - 3,02\times10^{-19}$ J

Note: $\Delta E < 0$; it is indeed an emission of energy. According to the Planck-Einstein relation:

$\Delta E = h.\ c\ \lambda$ and $\lambda = h.c/\Delta E$

$\lambda = 657$ nm

4.4. Ionization Energy

Ionization energy (Ei) is the energy required to move an electron from the ground state to an infinite distance, essentially removing the electron from the atom and sending it to an energy level of E = 0.

For example, the ionization energy (Ei) of the hydrogen atom is: $\boldsymbol{Ei} = \boldsymbol{E}\propto - \boldsymbol{E1}$ = 13.6 eV for the hydrogen atom, where $E\infty = 0$.

Note:

The excitation energy of the hydrogen atom is the energy required to move the electron from one orbit (n_1) to another (n_2), where $n_1 < n_2$.

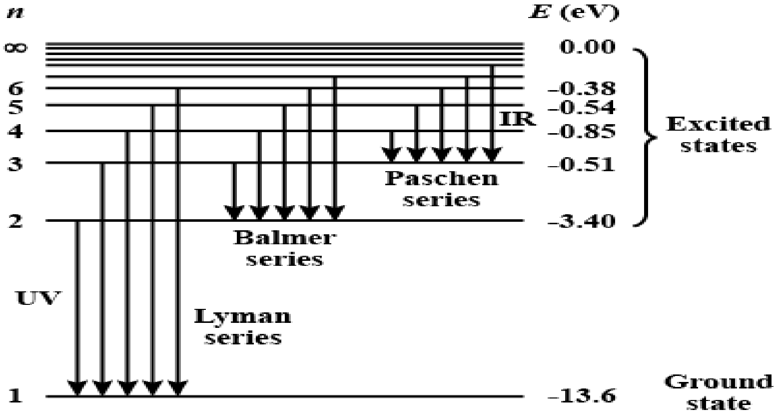


Figure IV.11: Energy Levels and Spectral Series of the Hydrogen Atom.

4.5. Hydrogen-like Ions

These are atoms that have lost all their electrons except one, making them similar to hydrogen in terms of the number of electrons. Therefore, Bohr's theory can be applied to these hydrogen-like ions.

Examples of hydrogen-like ions: $_2\mathbf{He}^+$, $_3\mathbf{Li}^{2+}$, $_4\mathbf{Be}^{+3}$

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

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

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

Their total energy is given by: $E_T = Z^2/ n^2. (-me^4 / 8\varepsilon_0{}^2h^2)$ $E_T = E_1.Z_2/ n^2$

The radius of an orbit with the nth rank of a hydrogen-like ion is:

$r = n^2/Z. (\varepsilon_0 h^2 / \pi me^2)$ or even $r = r_1 \times n^2 Z$

Here, r_1 = 0.529 Ångströms, which is the radius of the hydrogen atom in its ground state.

For hydrogen-like ions, the wavelength is expressed by the relation:

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

with $R_H = me^4 / 8\varepsilon_0{}^2h^3$: the Rydberg constant.

This relation allows for the calculation of different wavelengths. In general, multiple spectral series are found depending on the state in which the electron is located.

4.6. Shortcomings of the Bohr Model

Despite the arbitrariness of its two quantization hypotheses, the Bohr model enjoyed great success at the time because it was the only one that allowed for the calculation of the Rydberg constant and the retrieval of the emission lines of hydrogen-like ions.

Furthermore, this model, along with the involvement of Planck's constant in other theoretical explanations, prepared scientists to accept the idea that classical physics concepts were insufficient for understanding microscopic phenomena.

5. The Hydrogen Atom in Wave Mechanics

5.1. Wave-Particle Duality and the de Broglie Relation

In 1924, de Broglie proposed that each particle (corpuscle) with mass (m) and velocity (V) is associated with a wave of wavelength (λ).

$$\lambda = \frac{h}{P} = \frac{h}{mv}$$

This hypothesis is expressed through the de Broglie relation, which represents the wave-particle duality:

Where:

λ: Wavelength;

h: Planck's constant;

p: Momentum ;

m: Particle mass ;.

v: Particle velocity

Generally, the wave-like aspect of material bodies is often negligible at the macroscopic scale.

5.2. Heisenberg's Uncertainty Principle

It is impossible to precisely define both the position and velocity of a particle simultaneously. This is described by the following relation:

$$\Delta x\,.\,\Delta p \geq \frac{h}{4\pi} \Rightarrow \Delta v \geq \frac{h}{4\pi m \Delta x}$$

Where:

Δx: Uncertainty in position;

$\Delta p = m \times \Delta v$: Uncertainty in momentum.

Application Exercise

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

Solution:

$\Delta x = 1$ Å $= 10^{-10}$ m, me $= 9.11 \times 10^{-31}$ kg, $\Delta v \geq h / 4\pi m \Delta x$

Numerical Calculation:

$\Delta V \geq 6{,}625.\ 10^{-34} / 4\pi.\ 9{,}11.10^{-31} 10^{-10} \Leftrightarrow$ **$\Delta v \geq 5{,}79.10^{5}$ m/s**

The uncertainty in the velocity of the electron is significant.

This means that if we measure the position of the electron within 1 Ångström (which is a high level of precision), we will introduce a significant error in the measurement of its velocity, and vice versa.

5.3. Concept of Probability of Presence

In classical mechanics (Bohr's conception), studying the motion of an electron involves precisely determining its trajectory. However, in quantum mechanics, we discuss the probability of finding the electron at a certain point in space.

This spatial distribution is described by a function of the electron's coordinates called the wave function Ψ.

The probability of presence is: $dP = \Psi(x,y,z,t)^2\, dV$

The wave function Ψ must satisfy a certain normalization condition: $P = \int \Psi^2\, dV = 1$

It is said that the wave function is normalized.

5.4. Schrödinger's Equation for the Hydrogen Atom

Atomic orbitals are the wave functions of atomic electrons. In 1926, Schrödinger demonstrated that the wave function and the energy E are solutions to a second-order partial differential equation. The Schrödinger equation is written as:

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

This is the fundamental principle of quantum mechanics. Where:

E: Total energy of the electron, called the eigenvalue;

Ψ: Wave function, called the eigenfunction;

H is called the Hamiltonian operator of the hydrogen atom, and it is expressed as:

$H = (-h^2 / 8\pi^2 m)\, \Delta + V$; this is called the Hamiltonian operator of the hydrogen atom.

$\Delta = \partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2$; this is the Laplacian operator.

m: mass of the electron;

V: potential energy operator;

E: total energy of the electron, called the eigenvalue;

Ψ: wave function, called the eigenfunction.

This equation is the fundamental principle of quantum mechanics. Solving this equation leads to different values of E and Ψ:

$$E_n = -\frac{2\, m\, Z^2 k^2\, \pi^2 e^4}{n^2 h^2}$$

It is the same expression as that found by the Bohr model. With quantum mechanics, we can also explain the quantization of energy.

6. Quantum Numbers and the Concept of Atomic Orbitals

6.1. Quantum Numbers

The quantum state of an electron is defined by four quantum numbers.

6.1.1. Principal Quantum Number (n)

It characterizes the energy level occupied by the electron or the shell it occupies. It is sometimes designated by an uppercase letter.

n=1 Shell K

n=2 Shell L

n=3 Shell M

n=4 Shell N

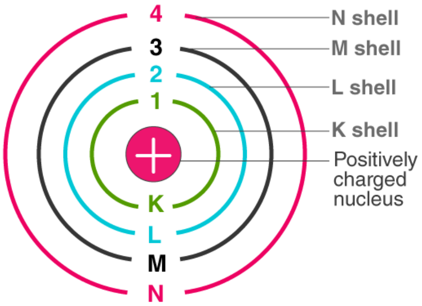


Figure IV.12: Representation of the Atom with the Principal Shells

6.1.2. Secondary Quantum Number (or Azimuthal) (l)

It characterizes the subshell occupied by the electron.

l=0 Subshell S

l=1 Subshell P

l=2 Subshell D

l=3 Subshell F

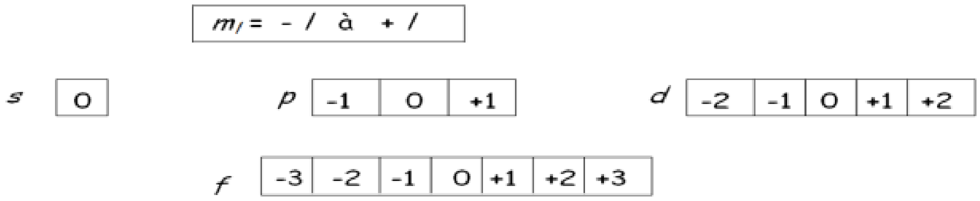
6.1.3. Magnetic Quantum Number (m)

It characterizes the quantum box occupied by the electron and determines its orientation in a magnetic field. Its value depends on the value of the secondary quantum number (l).

There are 2l+1 different values for m.

Graphically, this number is represented by a rectangle, and as many rectangles are represented as there are possible values of (m).

Example:



These three quantum numbers define a quantum box, and this box can contain two electrons. To distinguish between the two electrons, a fourth quantum number, spin (s), is introduced.

6.1.4. Spin Quantum Number (S)

It characterizes the intrinsic angular momentum of the electron and can only take two different values: $\pm\frac{1}{2}$

By convention:

$S = +\frac{1}{2}\uparrow \quad S = -\frac{1}{2}\downarrow$

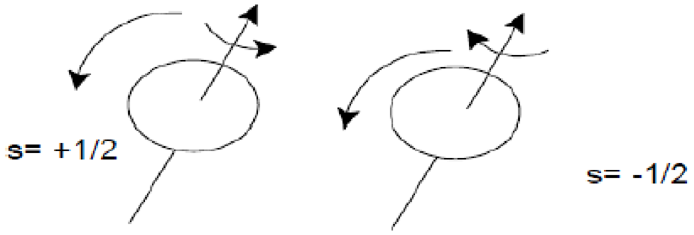


Figure IV.13: Electron Spin Movements.

7. Atomic Orbitals (AO)

7.1. s Atomic Orbital

These types of atomic orbitals are characterized by the following quantum numbers: l = 0 and m = 0. All these orbitals (ns) have spherical symmetry because the probability of finding the electron varies in the same way in all directions around the nucleus.

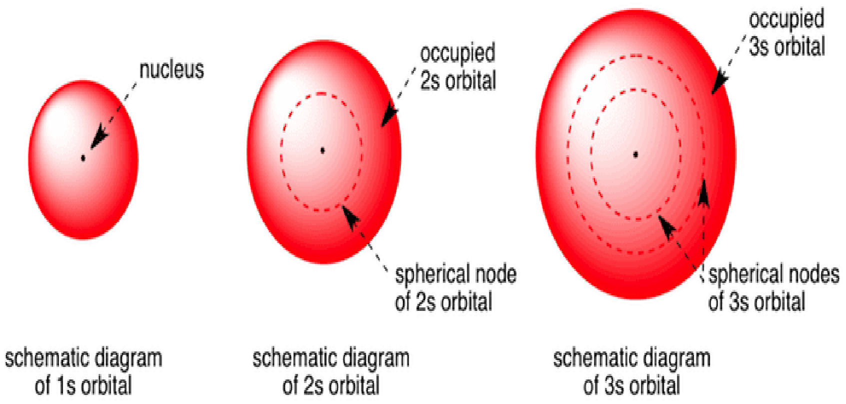


Figure IV.14: Shape of s-orbital.

7.2. p Atomic Orbital

For $l = 1$, we have $m = -1, 0, +1$, resulting in three p orbitals: px, py, and pz.

These orbitals have the same shape, but each one is elongated along one of the three perpendicular axes. These shapes are often referred to as dumbbells.

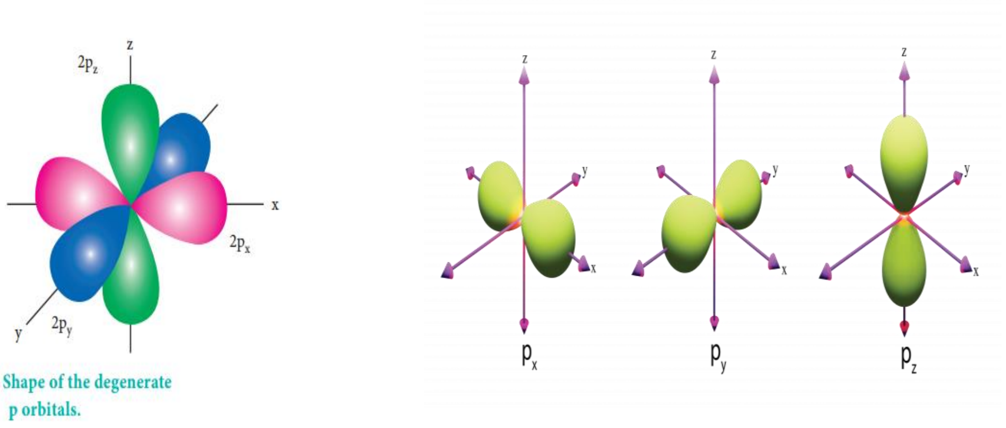


Figure IV.15: Shape of p-orbital.

7.3. d Atomic Orbital

When $l = 2$, m can take the following values: $m = (-2, -1, 0, 1, 2)$. Therefore, there are 5 d atomic orbitals. These orbitals have shapes resembling crossed dumbbells.

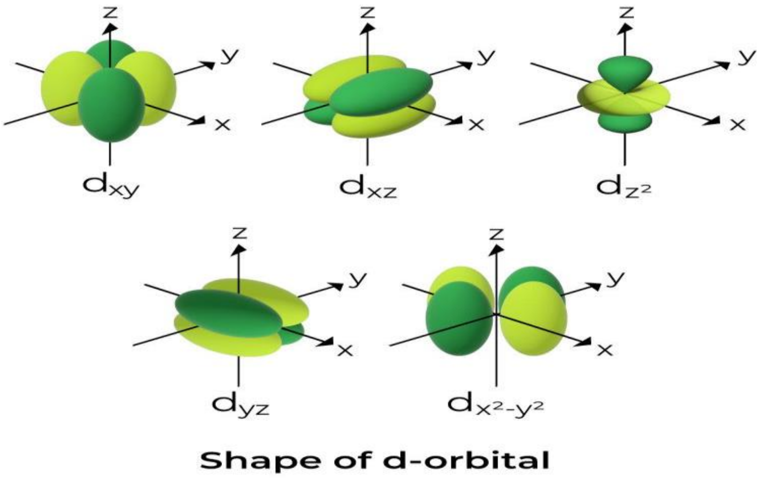


Figure IV.16: Shape of d-orbital.

7.4. f Atomic Orbital

If $l = 3$, m can take the values: $m = (-3, -2, -1, 0, +1, +2, +3)$, resulting in seven f orbitals.

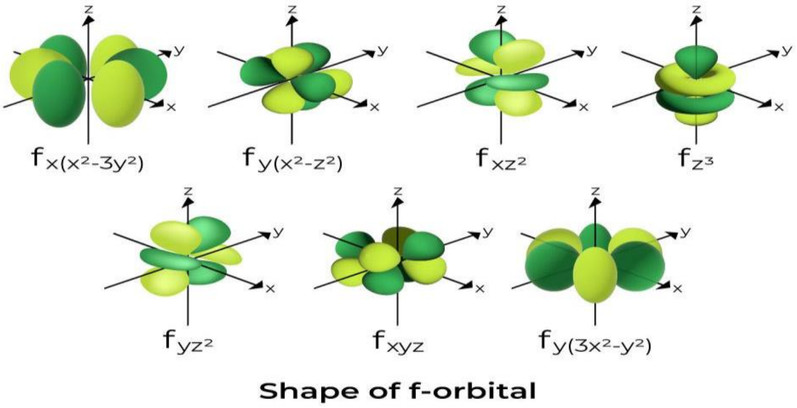


Figure IV.17: Shape of f-orbital.

7.5. Energy of Atomic Orbitals

The energy of a given orbital depends on its value of n. Therefore, all orbitals with the same value of n have the same energy; this is referred to as degeneracy.

The eigenvalues of the Schrödinger equation form a set of discrete energy levels (En) that depend only on the principal quantum number (n), which is an integer ranging from 1 to infinity: $E_n = -13.6(Z^2 / n^2)$ (eV).

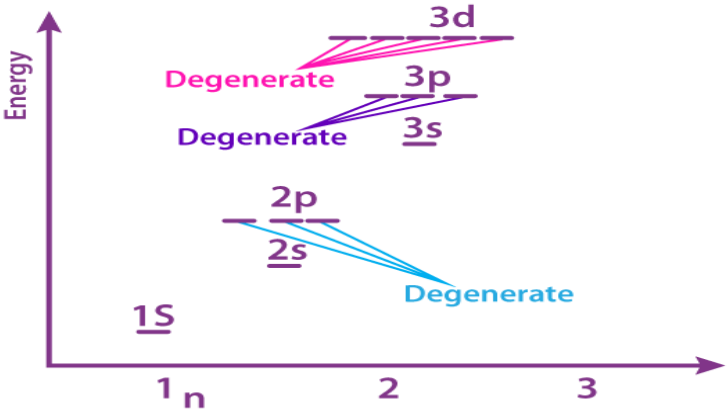


Figure IV.18: Degenerate Energy Levels of Atomic Orbitals.

8. Poly-Electronic Atom

In the case of a poly-electronic atom, each electron is subject to the attraction of the nucleus but also, to repulsive forces from the other electrons in the atom.

Rigorous resolution of the Schrödinger equation in this case is not possible, so approximation methods are used.

The Slater approximation involves replacing the atomic number (z) with an effective atomic number (z_{eff}) for each electron.

In poly-electronic atoms, due to interelectronic repulsions, the energy of orbitals varies in a specific order:

$E_{ns} < E_{np} < E_{nd} < E_{nf}$

For example, for the n = 3 shell: $E_{3s} < E_{3p} < E_{3d}$

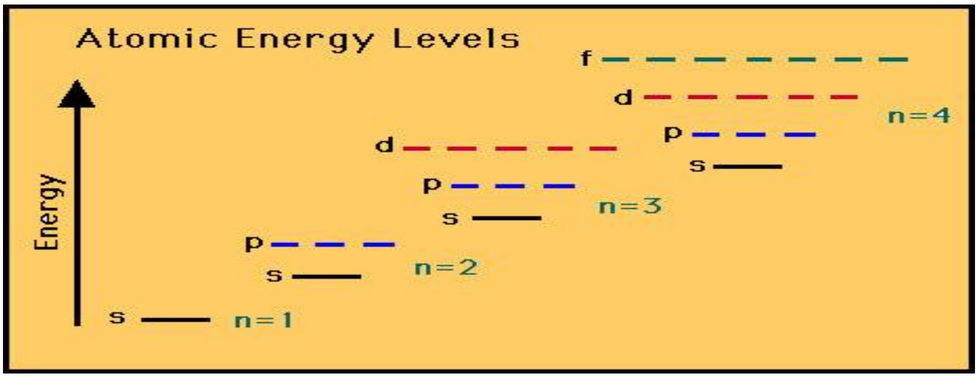


Figure IV.19: Energy Levels of Atomic Orbitals in a Poly-Electronic Atom.

9. Electron Configuration of the Atom

The electron configuration is constructed following the following empirical rules:

9.1. Building (or Filling) Rule

Electrons are distributed in a way that the atom has the lowest possible energy in its ground state. Orbitals are "filled" following the Pauli Exclusion principle, starting with the lowest energy orbitals and progressing gradually (Klechkowski's rule) until all electrons are used.

The energy of the atom is the sum of the hydrogen-like energies of individual electrons.

9.2. Klechkowski's Rule (Filling Order)

The ground state of the atom represents the lowest energy level and, therefore, the most stable state of the electron. Electrons will begin to occupy the lowest energy levels first until all available spaces are filled. The filling of shells and subshells is determined by Klechkowski's rule, which is based on the order of (n + l).

If n + l is the same, the subshell with the smallest n value will be filled first. For example, for 4p and 3p, both subshells have (n + l) = 4, but the smaller n value in 3p results in filling 3p before 4s.

Various shells and subshells are written in a table, with each row corresponding to a value of n.The filling is done along the diagonals.

The order of filling the subshells is then as follows:

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

This sequence follows the increasing order of (n + l).

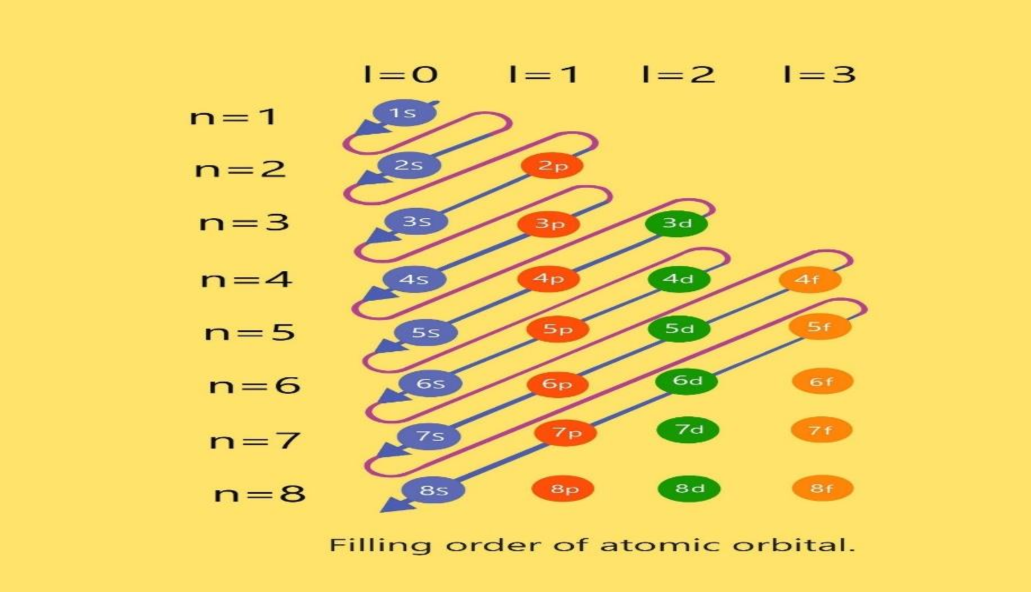


Figure IV.20: Klechkowski's rule.

9.2.1. Exceptions to Klechkowski's Rule

Starting from the n = 4 level, the filling of atomic orbitals does not strictly adhere to Klechkowski's rule.

Example:

Copper (^{29}Cu): The most stable configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^1$.

Chromium (^{24}Cr): The most stable configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$

The most stable configuration for chromium is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$.

These exceptions correspond to half-filling and full-filling of the 3d subshell.

They are explained by the small energy gap between the 4s and 3d orbitals.

9.3. Hund's Rule

When electrons can occupy orbitals of the same energy in different distinct ways, the state of lowest energy is the one where the maximum number of spins are parallel.

When a subshell is not complete, electrons occupy the maximum number of orbitals with the same spin.

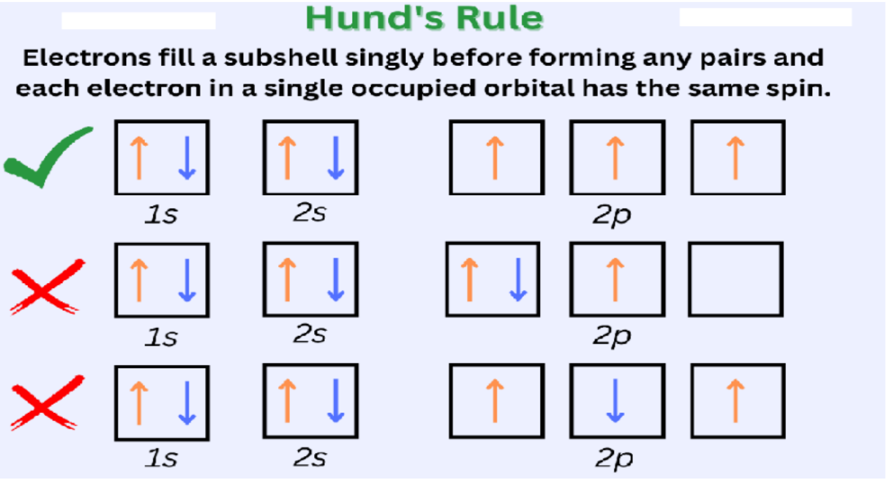


Figure IV.21: Hund's rule.

9.4. Pauli's Exclusion Principle

Pauli's Exclusion Principle states that for a given atom, two electrons cannot have all four quantum numbers identical.

Therefore, an atomic orbital (AO) defined by (n, l, m) can contain a maximum of two electrons with opposite spins.

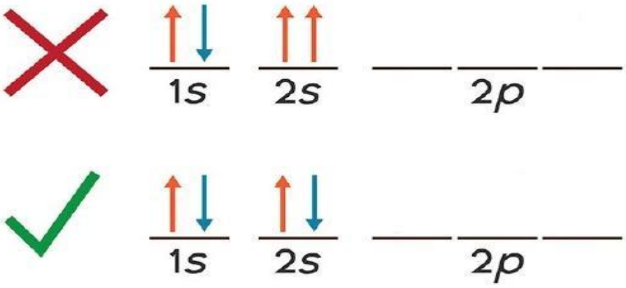


Figure IV.22: Pauli's exclusion principle.

9.5. Valence Shell

The electrons in the shell with the highest value of the principal quantum number (n) play a significant role in chemical reactions, especially in the formation of chemical bonds between atoms. This shell is called the outermost valence shell.

Example:

Lithium (^{3}Li): $1s^2\ 2s^1$, the valence shell is (n = 2), and the number of valence electrons is (1).

Carbon (^{6}C): $1s^2\ 2s^2\ 2p^2$, the valence shell is (n = 2), and the number of valence electrons is (4).

Examples of Applications:

Exercise 01:

Determine the complete electronic configurations of the following atomic species:

Na (Z=11), O (Z=8), Mg (Z=12), K^+ (Z=19), N^+ (Z=7), F^- (Z=9)

Solution:

Na (Z=11): $1s^2\ 2s^2\ 2p^6\ 3s^1$

O (Z=8): $1s^2\ 2s^2\ 2p^4$

Mg (Z=12): $1s^2\ 2s^2\ 2p^6\ 3s^2$

K^+ (Z=19): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

N^+ (Z=7): $1s^2\ 2s^2\ 2p^2$

F^- (Z=9): $1s^2\ 2s^2\ 2p^6$

Exercise 02:

1-Are the following sets of values for the quantum numbers characterizing an electron possible or not? Justify your answer.

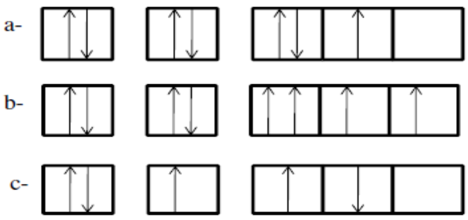
$n = 2, l = 0, m = 0$

$n = 2, l = 1, m = -1$

$n = 2, l = 2, m = 0$

d- $n = 4, l = 1, m = -2$

2-Here are electron structures written using quantum numbers. Correct those that are not accurate:



3-Given the electronic structures of the last electron shell of two elements, X and Y. Identify the ones that do not adhere to Klechkowski's rules and explain why.

X: $n S^2 (n-1) d^2$

Y: $n S^2 (n-1) d^9$

Solution:

1)

a) $n = 2, l = 0, m = 0$ - Yes ($0 \le l \le n - 1$ and $-l \le m \le l$)

b) $n = 2, l = 1, m = -1$ - Yes ($0 \le l \le n - 1$ and $-l \le m \le l$)

c) $n = 2, l = 2, m = 0$ - No ($0 \le l \le n - 1$)

d) $n = 4, l = 1, m = -2$ - No $(-l \leq m \leq l)$

2)

a) is not correct, Hund's rule is not followed.

b) is not correct, Pauli's exclusion principle is not followed.

c) is not correct, Hund's rule is not followed.

3)

a- is not correct, the electrons in the $(n-1)\ d^2$ subshell are closer to the nucleus than those in the $n\ S^2$ subshell.

b- is not correct, the electrons in the $(n-1)\ d^9$ subshell are closer to the nucleus than those in the $n\ S^2$ subshell, and in addition, the S subshell borrows an electron from the d subshell, making it $(n-1)\ d^{10}\ n\ S^1$.

Corrected Exercises

Exercise 1:

We have three photoelectric cells. The cathodes are respectively coated with Cesium (Cs), potassium (K), and Lithium (Li). The extraction energies E0 of an electron from these metals are given in the table below:

Metal	Cs	K	Li
E_0 (ev)	1,19	2,26	2,39

1- What do we call extraction energy?

2- Each cell is successively illuminated by monochromatic radiation with a wavelength of λ=590 nm.

a- Calculate, in eV, the energy carried by a photon.

b- With which of these cells do we obtain the photoelectric effect? Justify your answer.

c- Calculate the maximum speed of an electron at the exit of the cathode.

Data: $h=6,62\ 10^{-34}$ J.S, $C= 3.\ 10^{8}$ m/s, $m_{\text{electron}}= 9,109\ 10^{-31}$ kg, $1eV=1,6\ 10^{-19}$ J.

Exercise 2:

1. The photoelectric threshold wavelength of a lithium atom is 5200 Å. Does lithium emit electrons when exposed to radiation with wavelengths greater or less than 5200Å?
2. Calculate the extraction energy for this metal and express it in eV.
3. Calculate the energy of the electrons emitted by a lithium plate placed in a vacuum and illuminated by radiation with a wavelength of 4500Å.
4. To prevent this photoemission, to what potential should the lithium plate be raised?

Exercise 3:

Applying the Bohr model to the hydrogen atom. Calculate:

a. The energy required to move the electron from the ground state to the 3rd excited state.

b. The frequency of the emitted radiation when the electron transitions from the 3rd excited state to the 2nd excited state.

c. The wavelength required to ionize the electron from the 3rd excited state.

Exercise 4:

The electron of the hydrogen atom is excited to the n=4 level.

a. How many different spectral lines can be emitted when this electron returns to the n=1 level?

b. The photons of the lowest energy are emitted due to which electron transition?

c. The photons with the lowest frequency correspond to which electron transition?

d. The line with the shortest wavelength corresponds to which electron transition?

Exercise 5:

One of the lines of the Paschen series in the emission spectrum of the hydrogen atom has a wavelength λ=18750,8 Å. To which electron transition does this line correspond?

Data: E_1=-13,6 eV, h= 6,62 10^{-34} J.s, R_H=1,1 10^7 m^{-1}, C=3.10^8 m/s, 1eV=1,6 10^{-19} J.

Exercise 6:

The energy levels of the hydrogen atom are given by the relation:

$$E_n = \frac{-13.6}{n^2} \text{ (eV).}$$

Data**:** h = 6.62×10^{-34} J·s, c = 3.00×10^8 m·s^{-1}, 1 eV = 1.60×10^{-19} J, 1nm = 10^{-9} m

1. Calculate the values corresponding to the 4 lowest energy levels.
2. What is the ground state?
3. Consider the transition from level 3 to level 2.
   a. Is this a radiation emitted or absorbed?
   b. Calculate the wavelength corresponding to this transition.
4. The atom absorbs a photon with a wavelength λ = 121.7 nm. Which transition does this absorption cause?

Exercise 7:

1- The electron of a hydrogen atom in an excited state n' releases a photon with a wavelength of 1.88μm, then becomes ionized by receiving an energy of 151.10^{-8} MeV.

a- Deduce the corresponding wavelength for the ionization of this electron.

b- b- Determine n'.

2- A hydrogen-like ion ${}^{2.Z}_{Z}X^{n+}$ undergoes the same transition of the electron in this hydrogen atom by emitting energy equal to 23.89 eV.

a. What is this hydrogen-like ion?

b. Calculate the frequency of the radiation that would cause the ionization of the electron in this hydrogen-like ion.

Exercise 8:

We consider a Beryllium ion ${}^{9}_{4}Be^{3+}$.

1. Knowing that r_1(H)=0.53 Å, what are the radii corresponding to the K and L shells of this ion?

2. When a radiation of wavelength λ is applied to this ion, an electron transitions from the n=1 shell to the n=5 shell. Calculate the frequency of the absorbed radiation.
3. Calculate the fourth ionization energy of Be in its ground state. Compare this value with the first, second, and third ionization energies E_1 = 9,32 eV, E_2 = 18,21 eV, E_3 = 153,8 eV.
4. Which ions can be most easily obtained from the Be atom?

Exercise 9:

1- Among these combinations of quantum numbers, which ones are allowed?

a- n=1 ; ℓ= 1 ; m=0 ; s=1/2
b- n=2 ; ℓ= 0 ; m=0 ; s=-1/2
c- n=4 ; ℓ= 1 ; m=-1 ; s=0
d- n=0 ; ℓ= 0 ; m=0 ; s=1/2
e- n=3 ; ℓ= -2 ; m=-1 ; s=1/2
f- n=5 ; ℓ= 4 ; m=3 ; s=-1/2
g- n=2 ; ℓ= 1 ; m=0 ; s=1/2

2- What is the maximum number of electrons that can be associated with the*n*=3 value?
3- Provide the notation for the following atomic orbitals:
a. n=3 ; ℓ= 1 / b. n=4 ; ℓ= 0 / c. n=4; ℓ= 2 / d. n=5 ; ℓ= 3.

Exercise 10:

1- We consider an electron in a quantum state defined by *n*=4 and *m*=2. Are the following statements true?
a- This electron can be found in a d orbital.
b- This electron is necessarily in a d orbital.
c- This electron can be found in a 4p orbital.
d- This electron can have a spin quantum number *s*=−1/2.
e- This electron can have an angular momentum quantum number ℓ=5.

2- We consider an electron in the 4s state.
a- What are the quantum numbers characterizing this electron?
b- Provide in tabular form the values of the quantum numbers corresponding to *n*=4.

Correction
Exercise 1:

1- The ionization energy (Ei) is the energy required to move an electron from the ground state to an infinite distance, which is equivalent to removing the electron from the atom and sending it to an energy level of E = ∞.

2-

a. Calculation of energy carried by a photon:

$E = h.\nu = h.C/\lambda = 6{,}62\ 10^{-34}.3.10^{8}/590.10^{-9} = 3{,}366\ 10^{-19}\ J = 2{,}103$ eV.

b. To achieve the photoelectric effect, E must be greater than E_0 ($E>E_0$), hence the Cesium (Cs) cell is used to produce this effect.

c. Calculation of the maximum speed:

$E=E_0+Ec \Rightarrow Ec=E-E_0$

$Ec=2{,}103 - 1{,}19 = 0{,}913$ eV;

$Ec= m.v^2/2$ $\qquad V = \sqrt{\frac{2Ec}{m}} = \sqrt{\frac{2.0{,}913.\ 1{,}6\ 10^{-19}}{9{,}109.10^{-31}}} = 0{,}566\ 10^6$ m/s

Exercise 2:

1. Does lithium emit electrons when exposed to radiation with wavelengths greater or less than 5200 Å?

$E>E_0 \Rightarrow h.\nu > h\nu_0 \Rightarrow \nu > \nu_0 \Rightarrow C/\lambda > C/\lambda_0 \Rightarrow 1/\lambda > 1/\lambda_0$

Thus, $\lambda < \lambda_0$, i.e., the case where λ is smaller than λ_0 (5200Å).

2. Calculate the extraction energy (E_0) for lithium:

$E_0= h.\nu_0 = h.C/\lambda_0= 6{,}62\ 10^{-34}.3.10^{8}/5200.10^{-10} = 3{,}819 . 10^{-19}$ J= 2,38 eV.

3. Calculate the energy of the electrons emitted by a lithium plate illuminated by radiation with λ=4500Å:

$E= h.\nu = h.C/\lambda= 6{,}62\ 10^{-34}.3.10^{8}/4500.10^{-10} = 4{,}413.10^{-19}$ J= 2,758 eV.

4. The stopping potential (Vs) that will prevent photoemission:

$Ec_{max} = m.v^2_{max}/2 = e.V_0$

$E=E_0+Ec$, donc $Ec=E-E_0 = 2{,}758 - 2{,}38= 0{,}378$ eV$= 0{,}6048.10^{-19}$ J

$Ec_{max} = e.V_0 \Rightarrow V_0 = Ec_{max}/e = 0{,}6048.10^{-19}/1{,}6\ 10^{-19} = 0{,}378$ volts

The stopping potential corresponds to the voltage that must be applied between the electrodes of the plate to cancel out the kinetic energy of the electrons.

Exercise 3:

a. Energy required to move the electron from the ground state to the 3rd excited state:

$E= h.\nu = h.C/\lambda$ $\qquad 1/\lambda= R_H Z^2 (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ avce $n_2 > n_1$

$E= h.C.R_H Z^2 (\frac{1}{n_1^2} - \frac{1}{n_2^2}) = 6{,}62\ 10^{-34}.3.10^{8}\ 1{,}1\ 10^{7}\ 1^2 (1-\frac{1}{16}) = 20{,}48\ 10^{-19}$ J= 12,8 eV

b. Frequency of the emitted radiation when transitioning from the 3rd excited state to the 2nd excited state:

$1/\lambda = RH\ Z^2\ (\frac{1}{n_1^2} - \frac{1}{n_2^2}) = 1{,}1\ 10^7\ 1^2\ (\frac{1}{9} - \frac{1}{16}) = 0{,}0534\ 10^7\ m^{-1}$

$\nu = C/\lambda = 3.\ 10^8\ 0,\ 0534\ 10^7 = 0{,}1604\ 10^{15}\ s^{-1}$

c. Wavelength required to ionize the electron from the 3rd excited state:

$1/\lambda = RH\ Z^2\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ n2= infini donc $1/\lambda = \frac{RH\ Z^2}{n_1^2} = 1{,}1\ 10^7\ 1^2/\ 16 = 0{,}06875\ 10^7$

$\lambda = 14{,}5454\ 10^{-7}\ m = 1454\ nm.$

Exercise 4:

a. The number of different spectral lines can be emitted when the electron returns to the n=1 level:

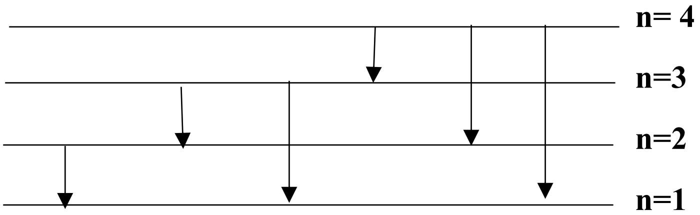
An electron at n=4 can transition to lower energy levels (n=3, n=2, and n=1) in multiple ways. The number of possible spectral lines can be calculated using the formula:

$$Number\ of\ lines = \frac{n(n-1)}{2}$$

Where n is the initial energy level (n==4).

$$Number\ of\ lines = \frac{4(4-1)}{2} = 6$$

A total of 6 different spectral lines can be emitted.



b, c et d :

lowest energy.	lowest frequency.	hortest wavelength.
$E = h.\nu = h.\ C/\lambda$ $E = h.\ C\ .\ RH\ Z^2\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $E = cost\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $E = cost\ (\frac{1}{n_1^2} - \frac{1}{4^2})$ $E = cost\ (\frac{1}{n_1^2} - 0{,}0625)$	$\nu = C/\lambda = C\ .\ RH\ Z^2\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $\nu = cost'\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $\nu = cost'\ (\frac{1}{n_1^2} - \frac{1}{4^2})$ $\nu = cost'\ (\frac{1}{n_1^2} - 0{,}0625)$	$1/\lambda = RH\ Z^2\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $\lambda \searrow \Rightarrow 1/\lambda \nearrow$ $1/\lambda = cost''\ (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $1/\lambda = cost''\ (\frac{1}{n_1^2} -0625)$

n	**n=4**	**n=3**	**n=2**	**n=1**
n²	**16**	**9**	**4**	**1**
1/n²	**1/16=0,0625**	**1/9=0,1111**	**¼=0,25**	**1**

Therefore, the transition that gives the lowest energy and the lowest frequency is the electronic transition n=4 to n=3, and the transition that gives the shortest wavelength is the electronic transition n=4 to n=1.

Exercise 5

Paschen series, so n=3. Emission spectrum: the electron transitions from a higher level to a lower level n=3.

$1/\lambda = R_H Z^2 (\frac{1}{n_1^2} - \frac{1}{n_2^2})$ $n_2 > n_1 \Rightarrow 1/\lambda = R_H Z^2 (\frac{1}{3^2} - \frac{1}{n_2^2})$

$$\frac{1}{18750{,}8\ 10^{-10}} = 1{,}1\ 10^7\ 1^2\ (\frac{1}{9} - \frac{1}{n_2^2})$$

and we calculate n_2

$n_2 = 4$

Therefore, the electron transition corresponds to the transition from n=4 to n=3 in the Paschen series of the hydrogen atom.

Exercise 6:

1. Energy levels of the hydrogen atom

$$n = 1 \Rightarrow E_1 = \frac{-13.6}{1^2} = -13.6\ (\text{eV}).$$

$$n = 2 \Rightarrow E_2 = \frac{-13.6}{2^2} = -3.4\ (\text{eV}).$$

$$n3 \Rightarrow E_3 = \frac{-13.6}{3^2} = -1.51\ (\text{eV}).$$

$$n = 4 \Rightarrow E_4 = \frac{-13.6}{4^2} = -0.85\ (\text{eV}).$$

2. What is the ground state: The ground state is the n=1 energy level (−13.6 eV).

3. Transition from n=3 to n=2:

a. The radiation is emitted during the n=3→n=2transition.

b. Wavelength of the emitted radiation:

$\Delta E = E_2 - E_3 = -3.4 - (-1.51) = -1.89\text{eV} = -3{,}02 \times 10^{-19}$ J.

According to the Planck-Einstein relation:

$$\Delta E = \frac{h \cdot c}{\lambda} \Rightarrow \lambda = \frac{h \cdot c}{\Delta E} = \frac{6.62\ 10^{-34}\ 3\ 10^8}{3.02\ 10^{-19}} = 675\ \text{nm}.$$

The wavelength of the emitted radiation is 657 nm.

4. The transition that causes this absorption:

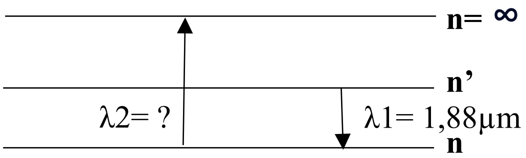
$$\Delta E = \frac{h \cdot c}{\lambda} \Rightarrow \lambda = \frac{h \cdot c}{\Delta E} = \frac{6.62\ 10^{-34}\ 3\ 10^8}{121.7\ 10^{-9}} = 1.63 \times 10^{-18}\text{J} = 10.2\ \text{eV}.$$

This energy corresponds to the transition from n=1 to n=2, as:

$E_{2\to1}=E_2-E_1=-3.4-(-13.6)=10.2$ eV.

The absorption of a 121.7nm photon causes a transition from n=1 to n=2.

Exercise 7



1.

a. The wavelength for the ionization of this electron.

$E_i=h\,.\,C/\lambda_2$ $\lambda_2=h.c/E_i$

$$\lambda_2=\frac{6{,}62\,10^{-34}\,.\,3.\,10^{8}}{151.\,10^{-8}\,.\,10^{6}\,.\,1{,}6\,.\,10^{-19}}$$

$\lambda_2=0{,}0822\;10^{-5}$ m=822 nm

b. Determine n′

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

$1/\lambda_1=R_H Z^2\left(\frac{1}{n^2}-\frac{1}{n'^2}\right)$ ………(1)

$1/\lambda_2=R_H Z^2\left(\frac{1}{n^2}-\frac{1}{n_\infty^2}\right)$ ………..(2)

(1)-(2) $\frac{1}{\lambda1}-\frac{1}{\lambda2}=R_H Z^2\left(-\frac{1}{n'^2}\right)$ $\frac{1}{\lambda1}-\frac{1}{\lambda2}=-\frac{R_H Z^2}{n'^2}$ n'=4

2. The hydrogen-like ion undergoes the same transition by emitting an energy of E=23.89 eV, so it is the transition from n′ to n. It is necessary to calculate n using the relation (1).

$1/\lambda_1=R_H Z^2\left(\frac{1}{n^2}-\frac{1}{n'^2}\right)$, We can calculate n (n=3)

a. The nature of the hydrogen-like ion

$E=h\,.C/\lambda=h.\,C\,.\,R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$ $n_2>n_1$ (n_1=n=3 et n_2=n'=4)

We can calculate Z (Z=6)

Therefore, the hydrogen-like ion is ${}^{12}_{6}X^{+5}$ (${}^{12}_{6}C^{+5}$)

b. The ionization frequency

$\nu=C/\lambda=C\,.\,R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n\infty}\right)$ with n_1=3 and Z=6

$\nu=2{,}2\;10^{15}\;S^{-1}=2{,}2\;10^{15}$ Hz.

Exercise 8:

1. The corresponding radii to the K and L shells of the Beryllium ion:

For hydrogen-like ions, the radius of an electron in the nth shell can be calculated using the formula:

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

r_1(H)=0.53A° is the radius for the hydrogen atom in the n=1 shell,

For the Beryllium ion ${}^{9}_{4}\mathrm{Be}^{3+}$ Z=4.

$$\text{K shell (n = 1)}: r_1 = \frac{1^2 \cdot 0.53}{4} = 40.53\text{Å} = 0.1325\text{Å}$$

$$\text{L shell (n = 2)}: r_2 = \frac{2^2 \cdot 0.53}{4} = 0.53\text{Å}.$$

2. The frequency of the absorbed radiation:

$$\upsilon = \frac{C}{\lambda} = C\, R_H\; Z^2\, (\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

For the Beryllium ion ${}^{9}_{4}\mathrm{Be}^{3+}$ Z=4.

$$\upsilon = 3.10^8\; 1.1\; 10^7 16\left(\frac{1}{1^2} - \frac{1}{5^2}\right) = 50{,}688\; 10^{15}\ \text{Hz}.$$

3. The fourth ionization energy of ${}^{9}_{4}\mathrm{Be}^{3+}$:

The ionization energy of an electron in a hydrogen-like ion is given by:

$$\mathrm{E_i} = \frac{13.6\ \mathrm{Z}^2}{\mathrm{n}^2}\ \mathrm{eV}$$

For the fourth ionization energy of Be in its ground state (n=1, Z=4):

$$\mathrm{E_i} = \frac{13.6\ 4^2}{1^2}\ \mathrm{eV} = 217.6\ eV$$

The fourth ionization energy is much higher than the first three due to the increasing nuclear charge experienced by the electron as more electrons are removed.

4. Easily obtainable ions of Be

The energy required to remove each successive electron increases significantly. The first two ionizations (E_1=9.32 and E_2=18.21 eV) are relatively low, making ${}^{9}_{4}\mathrm{Be}^{+}$ and ${}^{9}_{4}\mathrm{Be}^{2+}$the most easily obtainable ions.

Exercise 9:

1. The allowed combinations are: b, g and f.

2. The maximum number of electrons = $2, n^2 = 2 .3^2=18$ electrons.

3. The notation of atomic orbitals:

a: 3p;
b: 4s;
c: 4d;
d: 5f.

Exercise 10:

1. Analyze of statements: a: True, b: False, c: False, d: True, e: False

2. a. The quantum numbers characterizing this electron

$n=4$ $\ell=0$ $m=0$ $s= +1/2$ or $-1/2$

b**. The values of the quantum numbers corresponding to n=4n = 4n=4 are:**

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

Chapter V:
Periodic Classification of Elements

1.Introduction

The study of the electronic structure of atoms allows for a deeper understanding of the periodic classification of elements, also known as Mendeleev's periodic classification, established in 1869.

The periodic table remains the most important means of comparison among various chemical elements. It facilitates the understanding of groups of elements, their associated chemical properties, and their structures. Furthermore, this classification enables the determination of compound formulas and the types of bonds uniting atoms in molecules.

2.Periodic Classification by D. Mendeleev

In 1869, D. Mendeleev classified the periodicity of the properties of 63chemical elements known at that time in a table based on the ascending order of their atomic masses.

This periodic table not only facilitates the comparison between elements but also has allowed for a better understanding of the relationship between chemical properties and their atomic structures.

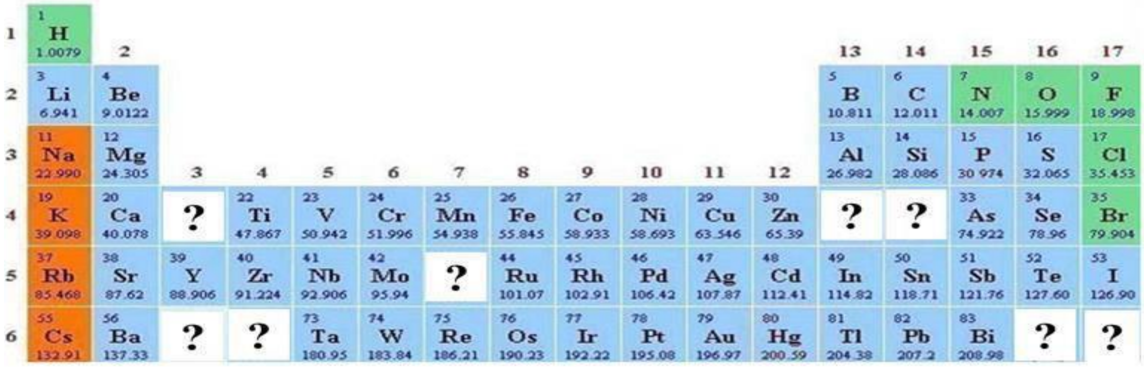


Figure V.1: Periodic Table of D. Mendeleev in 1869.

3.Modern Periodic Classification

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

This classification is represented in a table with seven (7) rows (periods) and 18 columns (groups or subgroups).

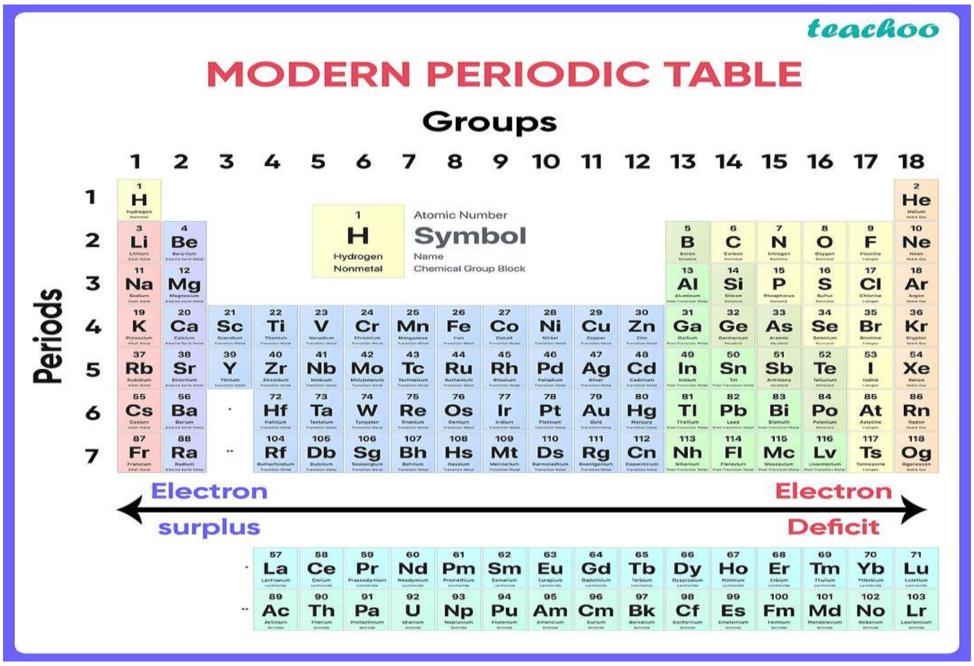


Figure V.2: Modern Periodic Table.

The periodic table is divided into:

Blocks: Elements are placed in three blocks:

Block (S): Corresponds to the filling of the subshell (ns). The s-block consists of elements found in columns 1 (alkali metals) and 2 (alkaline earth metals) of the periodic table, as well as hydrogen and helium. They are called so because their highest (in energy) occupied orbital is of type s.

Block (P): The p-block corresponds to the filling of the *np* subshell. It consists of elements located in columns 13 to 18 of the periodic table. These elements are so named because their highest-energy occupied orbitals are p orbitals. The p-block includes the boron family (column 13), the carbon family (column 14), the pnictogens (column 15), the chalcogens (column 16), the halogens (column 17), and the noble gases (column 18), excluding helium, which belongs to the s-block.

Block (d): Corresponds to the filling of the subshell ((n-1) d). The d-block consists of elements found in columns 3 to 12 of the periodic table. They are called so because the highest (in energy) occupied orbital is of type d.

Block (f): Corresponds to the filling of the subshell ((n-2) f). The f-block consists of internal transition elements of the periodic table: the lanthanides and actinides. They are called so because the highest (in energy) occupied orbital of these atoms is of type f.

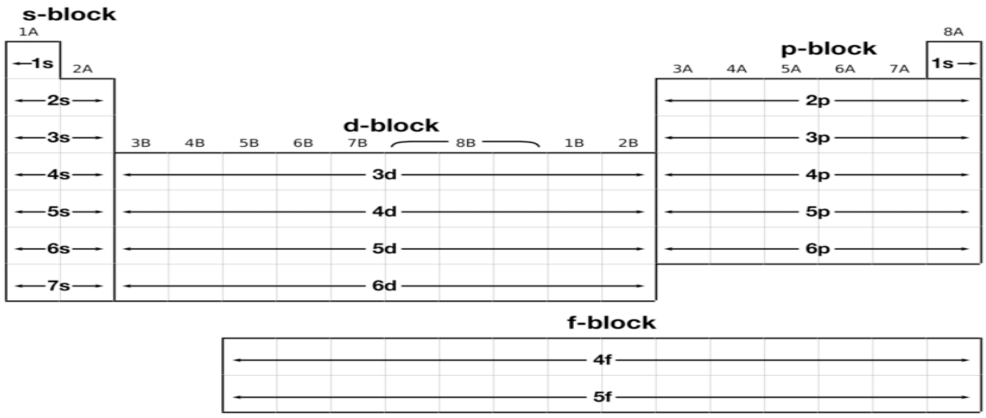


Figure V.3: Different Blocks of the Periodic Table.

Periods (Rows): A period corresponds to an electron shell identified by its principal quantum number, denoted as *n*. There are seven electron shells in the ground state; therefore, the periodic table contains seven periods.

Groups (Columns): There are eighteen columns, including Eight in subgroup A ten in subgroup B Elements of the same family have the same number of valence electrons; the family number corresponds to the number of valence electrons. Each subgroup consists of 8 groups, as shown in Figure. The group is symbolized by Roman numerals (I-VIII). By definition, the group represents the valence electrons.

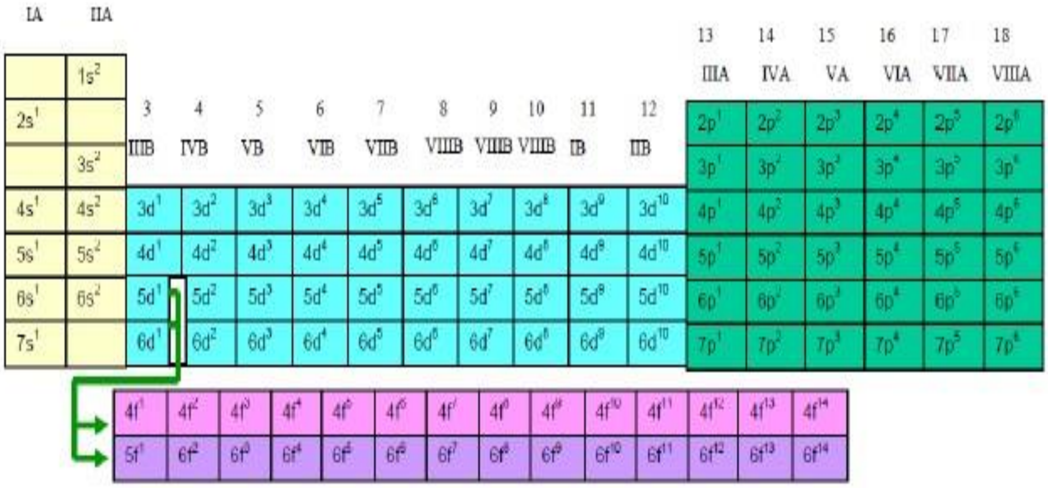


Figure V.4: Periodic Table Groups and Periods.

Subgroup A:

The eight families are called main groups, numbered from IA to VIIIA, represented by two blocks, s and p.

An element belongs to subgroup A if its valence electrons are distributed in the subshells (ns^x), $(ns^x np^y)$, or $(ns^x(n-1)d^{10}np^y)$, where $x$and $y$are both different from 0.

Table V.1: Electron Configurations and Example Elements of Subgroup A (Main Group Elements)

Group	Electron configuration	Example elements
1(IA)	ns^1	Na, K.
2(IIA)	ns^2	Mg, Ca.
13(IIIA)	ns^2np^1	Al, Ga.
14(IVA)	ns^2np^2	Si, Ge.
15(VA)	ns^2np^3	P, As.
16(VIA)	ns^2np^4	S, Se.
17(VIIA)	ns^2np^5	Cl, Br.
18(VIIIA)	ns^2np^6	Ar, Ne.

Subgroup B:

Families located between IIA and IIIA, represented by the d-block (transition elements).
An element belongs to subgroup B if its valence electrons are distributed in the shell ns^2(n-1) dx np^0, with x ranging from 1 to 10, or ns (n-2) f (n-1) d np^0. (the f subshell appears from n=6 onwards).

Table V.2: Electron Configurations and Example Elements of Group B (Transition Elements)

Group	Electron configuration	Example elements
3(IIIB)	$[Ar]4s^23d^1$	Sc, Y, La.
4(IVB)	$[Ar]4s^23d^2$	Ti, Zr, Hf.
5(VB)	$[Ar]4s^23d^3$	V, Nb, Ta.
6(VIB)	$[Ar]4s^13d^5$ (Cr exception)	Cr, Mo, W.
7(VIIB)	$[Ar]4s^23d^5$	Mn, Tc, Re.
8(VIIIB)	$[Ar]4s^23d^6$	Fe, Ru, Os.
9(VIIIB)	$[Ar]4s^23d^7$	Co, Rh, Ir.
10(VIIIB)	$[Ar]4s^23d^8$	Ni, Pd, Pt.
11(IB)	$[Ar]4s^13d^{10}$ (Cu exception)	Cu, Ag, Au.
12(IIB)	$[Ar]4s^23d^{10}$	Zn, Cd, Hg.

General Notes on Exceptions:

These exceptions occur because a **half-filled (d^5)** or **fully filled (d^{10})** subshell is more stable than expected from strict application of the Aufbau principle.

They mostly appear in **transition metals** and **lanthanides/actinides** where the energy difference between subshells is minimal.

Key Exceptions in Electron Configurations

1. **Chromium (Cr, Z=24)**
   a. **Expected:** [Ar] $4s^2$ $3d^4$
   b. **Actual:** [Ar] $4s^1$ $3d^5$
   c. **Reason:** Stability of a half-filled 3d subshell.
2. **Copper (Cu, Z=29)**
   a. **Expected:** [Ar] $4s^2$ $3d^9$
   b. **Actual:** [Ar] $4s^1$ $3d^{10}$
   c. **Reason:** Stability of a fully filled 3d subshell.
3. **Niobium (Nb, Z=41)**
   a. **Expected:** [Kr] $5s^2$ $4d^3$
   b. **Actual:** [Kr] $5s^1$ $4d^4$
   c. **Reason:** Stability of partially filled d-orbitals.
4. **Molybdenum (Mo, Z=42)**
   a. **Expected:** [Kr] $5s^2$ $4d^4$
   b. **Actual:** [Kr] $5s^1$ $4d^5$
   c. **Reason:** Stability of a half-filled 4d subshell.
5. **Ruthenium (Ru, Z=44)**
   a. **Expected:** [Kr] $5s^2$ $4d^6$
   b. **Actual:** [Kr] $5s^1$ $4d^7$
   c. **Reason:** Enhanced stability by breaking symmetry.

6.Rhodium (Rh, Z=45)
   a. **Expected:** [Kr] $5s^2$ $4d^7$
   b. **Actual:** [Kr] $5s^1$ $4d^8$
   c. **Reason:** Enhanced stability from increased 4d electron density.

7.Palladium (Pd, Z=46)
   a. **Expected:** [Kr] $5s^2$ $4d^8$
   b. **Actual:** [Kr] $4d^{10}$
   c. **Reason:** Completely filled d-orbitals compensate for empty 5s orbital.

8.Silver (Ag, Z=47)

a. **Expected:** [Kr] $5s^2\ 4d^9$

b. **Actual:** [Kr] $5s^1\ 4d^{10}$

c. **Reason:** Stability of a fully filled 4d subshell.

9.Platinum (Pt, Z=78)

a. **Expected:** [Xe] $6s^2\ 4f^{14}\ 5d^8$

b. **Actual:** [Xe] $6s^1\ 4f^{14}\ 5d^9$

c. **Reason:** Stability from filling the d-orbital closer to completion.

10.Gold (Au, Z=79)

a. **Expected:** [Xe] $6s^2\ 4f^{14}\ 5d^9$

b. **Actual:** [Xe] $6s^1\ 4f^{14}\ 5d^{10}$

c. **Reason:** Stability of a fully filled 5d subshell.

Example:

Find the period, group, and subgroup of the following elements:$_{28}$Ni, $_{30}$Zn, $_{53}$I et $_{79}$Au.

Solution:

$_{28}$Ni (Nickel):

Electron Configuration: $_{18}$[Ar] $4s^2\ 3d^8\ 4p^0$

Nickel belongs to the fourth period, Group VIII, Subgroup B, Column 10.

$_{30}$Zn (Zinc):

Electron Configuration: $_{18}$[Ar] $4s^2\ 3d^{10}\ 4p^0$

Zinc belongs to the fourth period, Group II, Subgroup B, Column 12.

$_{53}$I (Iodine):

Electron Configuration: $_{36}$[Kr] $5s^2\ 4d^{10}\ 5p^5$

Iodine belongs to the fifth period, Group VII, Subgroup A because the d subshell is completely filled.

$_{79}$Au (Gold):

Electron Configuration (initial): $_{54}$[Xe] $6s^2\ 4f^{14}\ 5d^9\ 6p^0$

Given configuration is unstable, so it becomes: 54[Xe] $6s^1\ 4f^{14}\ 5d^{10}\ 6p^0$ Gold belongs to the sixth period, Group I, Subgroup B, Column 11.

3.1. Element Families

The periodic table is composed of several families, and each family comprises atoms with the same valence shell. The main families on the periodic table include:

Alkali Metals Family (Column 1): Group IA, with an electron configuration of the type ns^1.

Alkaline Earth Metals Family (Column 2): Group IIA, with an electron configuration of ns^2.

Chalcogens Family (Column 13): Group IIIA, with an electron configuration of ns^2np^1.

Halogens Family (Column 17): Group VIIA, with an electron configuration of ns^2np^5.

Noble Gases Family (Column 18): Group VIIIA, with an electron configuration of ns^2np^6.

Metalloids (Semiconductors) Family: These elements form a boundary that separates metals and non-metals. It includes all elements from the 13th column to the 18th column. These elements share properties with non- metals but conduct electric current to varying degrees. Examples include Si, Ge, As, and Sb.

Transition Elements Family (Columns 3 to 11): These elements have incompletely filled (d) orbitals.

Triads Family (Group VIIIB): Consists of triads of elements.

Rare Earth Elements Family: Involves f-orbital elements, with two types in this family: Lanthanides, corresponding to elements in the 6th period with $57 \leq Z \leq 71$, and Actinides, concerning atoms in the 7th period with $89 \leq Z \leq 103$.

3.2. Metals and Non-metals

3.2.1 Sanderson's Rule

An element is considered metallic if the number of electrons in its highest energy level (n) is less than or equal to its period number, except for Hydrogen (H) and Germanium (Ge).

For example:

$_{13}Al$: [Ne] $3s^23p^1$. The number of electrons in the valence shell is 3, and the period of Al is also 3 ($3 \leq 3$). Therefore, Al is a metal.

$_{83}Bi$: [Xe] $4f^{14}5d^{10}6s^26p^3$. In this case, the number of electrons in the valence shell is 5, and the period of Bi is 6 ($5 < 6$). Therefore, Bi is a metal.

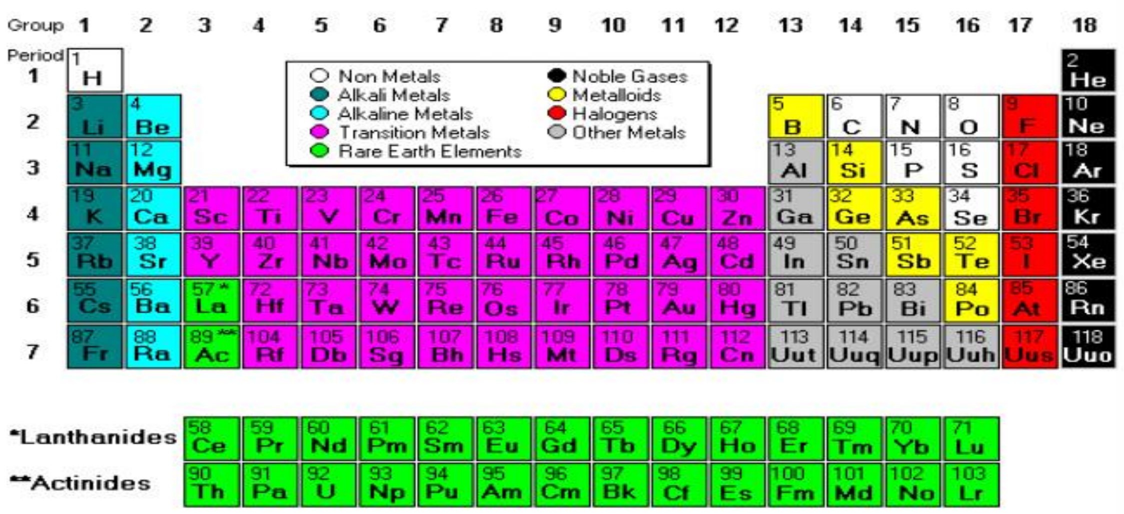


Figure V.5: Metals and Non-metals.

4. Evolution and Periodicity of Physico-Chemical Properties of Elements

Each group is characterized by periodic properties such as:

4.1. Atomic Radius

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

Across a period: As the atomic number (Z) increases, the atomic radius (ra) decreases.

Down a column: As the atomic number (Z) increases, the atomic radius (ra) increases

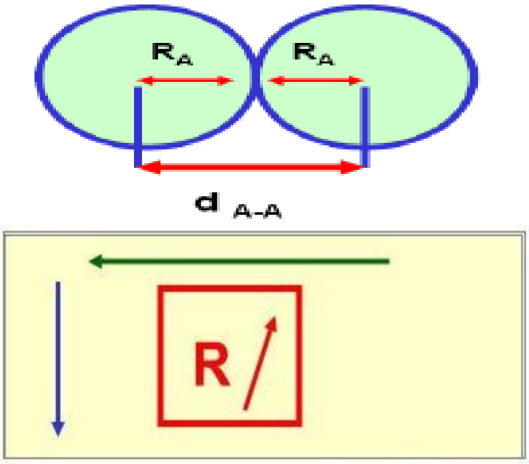


Figure V.6: Direction of Atomic Radius Increase.

Explanation:

When moving from left to right across a period, the nuclear charge increases, leading to an increase in nuclear attraction. Consequently, the atomic radii of elements decrease within a period from left to right.

When descending a column, the nuclear charge increases, causing an increase in nuclear attraction. However, the atomic radii do not decrease as expected because the outermost electrons are accommodated in new shells, generating an effect that outweighs nuclear attraction. Therefore, the atomic radii of elements increase within a column from top to bottom.

4.1.1. Ionic Radius (ri)

In general:

Cations are smaller than their parent atoms: ri (cation) < ra.

Anions are larger than their parent atoms: ri (anion) > ra.

For ions with the same electron configuration (e.g., S^{2-}, Cl^-, K^+, Ca^{2+}, Ti^{4+}), if Z increases, ri decreases.

At equal charges, the ionic radius varies in the same direction as the atomic radius: if Z increases, r_i decreases.

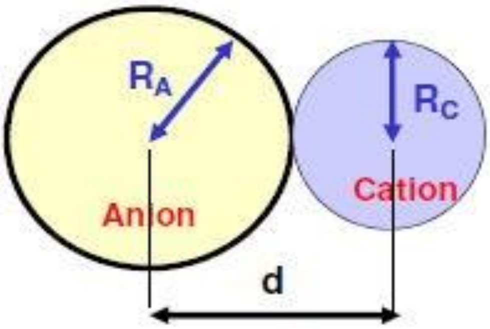


Figure V.7: Internuclear Distance.

If we express the ratio Ra / Rc, we have: $Ra/Rc = (k \times (na^2 / Zeffa)) / (k \times (nc^2 / Zeffc)) = Ra/Rc = k \times na^2 / Zeffa \times k \times nc^2 / Zeffc = Ra/Rc = na^2 / nc^2 \times Zeffc / Zeffa$.

Let's define: $K = na^2 / nc^2 \times Zeffc / Zeffa$, leading to $Ra = K \times Rc$.

In an ionic solid, Pauling assumed two spherical ions in contact, and the internuclear distance in the crystal is then simply the sum of the two ionic radii: $d = Ra + Rc$.

Thus, $d = K \times Rc + Ra$ leads to $d = Rc \times (k + 1)$, and $Rc = d / (k + 1)$, where $Rc = k \times d / (k+1)$.

Note:

For ions with the same electron configuration: if Zeff increases, ri decreases. At equal charges, the ionic radius varies in the same direction as the atomic radius: if Zeff increases, ri decreases.

4.2. Ionization Energy (IE)

Ionization energy is the energy required to remove an electron from an atom (or ion) in its ground state and in the gaseous state. Ionization energy varies inversely with atomic radius:

Across a period: If Z increases, EI increases.

Within a group: If Z increases, EI decreases.

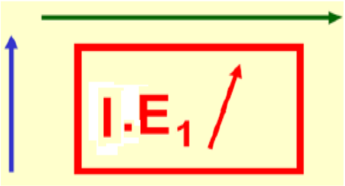


Figure V.8: Direction of Ionization Energy Increase (IE).

Explanation:

When moving from left to right across a period, the number of outermost electrons increases. Consequently, the nuclear attraction toward these electrons also increases. The higher this attraction, the more difficult it is to remove one of these electrons. Therefore, the first ionization energy increases within a period from left to right.

When descending a column, the electron to be removed is increasingly farther from the nucleus of the atom. Consequently, the nuclear attraction toward this electron decreases. The weaker this attraction, the easier it is to remove the electron. Therefore, the first ionization energy decreases within a column from top to bottom.

4.3. Electron Affinity

Definition:

Electron affinity (Ae) is the difference between the total energy of the atom and the energy released when the atom captures an electron (it is energy provided to oxidize).

$Ae = E(x) - E(x^-)$

$X + 1e \rightarrow X^- + A$ (electron affinity)

Example:

AH: $(H + 1e \rightarrow H^-)$ $Ae = 0.75$ eV.

Electron affinity increases across a period from left to right; however, it varies very little when descending a group.

4.4. Electronegativity

Electronegativity is the ability of an element to attract an electron.

An element that readily loses one or more electrons is referred to as electropositive.

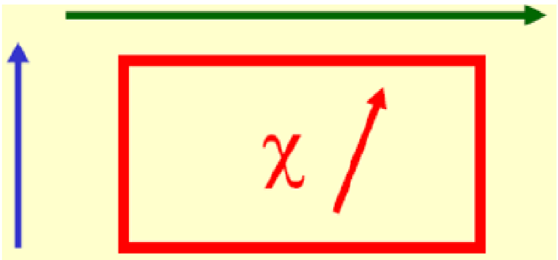


Figure V.9: Direction of Electronegativity Increase.

Electronegativity varies inversely with atomic radius, similar to ionization energy. The greater the electron affinity, the more energy is released when an atom captures an electron, making the capture more stable. A negative electron affinity means that energy must be supplied to the atom to remove an electron.

There are three different scales to measure electronegativity:

Mulliken Scale;

Pauling Scale;

Allred and Rochow Scale.

4.4.1. Mulliken Scale

Originally, Mulliken defined electronegativity as the average of the first ionization energy and the electron affinity of the element. An element with high electronegativity strongly attracts electrons, making it difficult to remove one (high first ionization energy) and easy to add one (high electron affinity).

$Xm = ½ (IE_1 – A_e)$

In this scale, the electronegativity difference between two elements is evaluated by the formula:

$(\Delta x)^2 = E_{AB} - (E_{AA} - E_{BB})^{1/2}$

Here, E_{AB}, E_{AA}, and E_{BB} are the energies of the A-B, A-A, and B-B bond s expressed in eV. Fluorine is the reference element to which Pauling assigned an electronegativity of $X_F = 4$.

4.4.2. Effective Charge

For a polyatomic atom, the outer electron, for example, is attracted by the nucleus (Z) but is repelled by all internal electrons (albeit not equally). This phenomenon is known as the shielding effect.

This outer electron (ej) is attracted not by the charge Z of the nucleus but by an effective charge Z_{eff} whose calculation takes into account the repulsions of internal electrons according to the Slater's rule.

Slater's Rule: This rule provides values for screening coefficients and allows the calculation of the effective atomic number (z_{eff}, where $z_{eff} < z$).

Consequently, it influences the atomic radius (ra), energy (En), and the potential for the first ionization (PI1).

$zeff = z - \sigma ij$

Here, σij represents the screening constant.

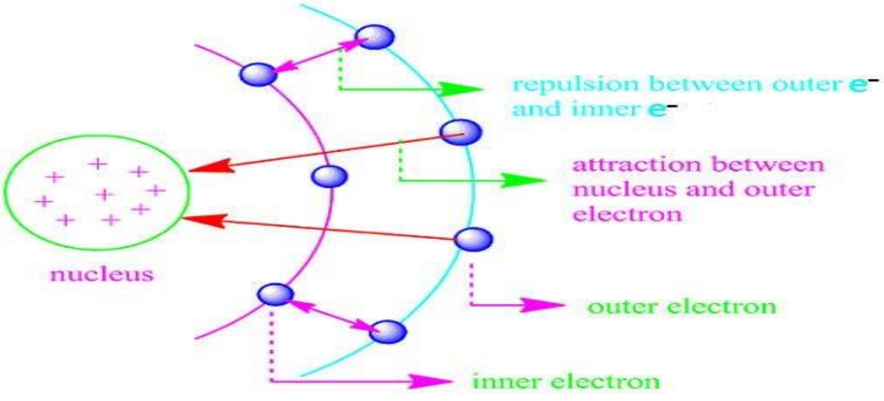


Figure V.10: Representation of Slater's Rule.

4.4.3. Screening Constant

Consider an electron (ei) in a polyatomic atom. It interacts with the nucleus and all the other electrons.

Its attraction to the nucleus's charge Z_{eff} is diminished by the repulsion of the other electrons. These other electrons act as a screen to the nucleus's attraction on the electron ei. It is as if a diminished charge Zeff is acting on ei, where Z_{eff} is an effective atomic number less than Z. This Z_{eff} is even smaller than Z when there are many electrons between ei and the nucleus, meaning ei is more external.

To estimate Z_{eff}, one must subtract the effects of various electrons other than e_i from Z. Empirically, a screening constant σ_{ij} is assigned to each electron e_j located between ei and the nucleus.

This constant depends on ej and also on e_i, as it is more significant when ej is close to the nucleus and e_i is far from the nucleus.

Zero values are assigned to the screening constants of electrons e_j placed farther from the nucleus than electron e_i. These values (see Table V.3) have been empirically determined through an average over several atoms based on experimental ionization energies.

It can be expressed as: $EI = 13,6 \times Z_{ef}^2 / n^2$

Here, EI represents the ionization energy, Zeff is the effective atomic number, and n is the principal quantum number.

Table V.3: Values of σij (Screening of e_i by e_j)

		e_j							
		1s	2s,2p	3s,3p	3d	4s4p	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
	4s4p	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

Examples: Calculate the effective atomic number of: ${}_6C$ and ${}_{17}Cl$

${}_6C : 1S^2\ 2S^2\ 2p^2$

$Zeff = 6 - (3 \times 0,35 + 2 \times 0,85) \Rightarrow z_{eff} = 3,25$

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

Z_{eff} = 17- (6 × 0.35) – (8 × 0.85) – (2 × 1) = 6.1

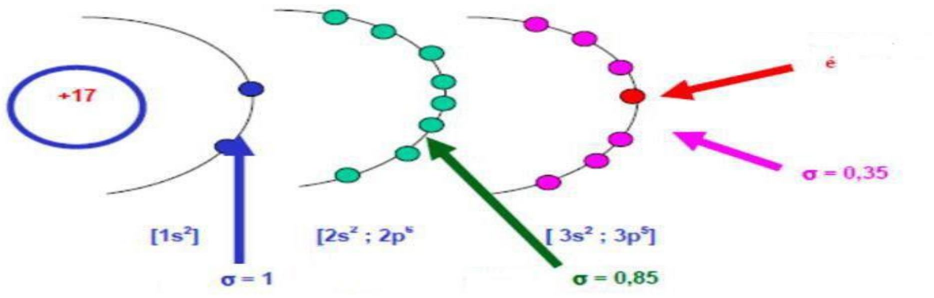


Figure V.11: The Z effective of $_{17}$Cl.

Exercise of application:

Consider the following atoms: C(6), P(15), V(23), Cr(24), Co(27), Zn(30) and Ge (32),

1. Provide the location of these elements in the periodic table (indicate the group and period), specify the core electrons and valence electrons, as well as the number of lone electrons.

2. Classify these elements in ascending order for elements belonging to the same period, and then within the same group with respect to their:

   a. Ionization energy.
   b. Atomic radius
   c. Electronegativity

Solution:

Element	**Atomic Number**	**Electronic Configuration**	**Period**	**Group**	**Core Electrons**	**Valence Electrons**	**Lone Electrons**
C	6	$1s^2\ 2s^2\ 2p^2$	2	IV_A	2	4	2
P	15	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	3	V_A	10	5	3
V	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	3	V_B	18	5	3
Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 3d^5$	4	VI_B	18	6	6
Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	4	VIII_B	18	9	3
Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^{10}$	4	II_B	18	2	0
Ge	32	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$	4	IV_A	28	4	2

Ranking:

In a column: (from top to bottom) As Z increases: atomic radius (ra) increases Ionization energy and electronegativity decrease, In a period: (from left to right) As Z increases: atomic radius (ra) decreases; Ionization energy (EI) and electronegativity increase;

a. Ionization energy:

   EI (V) < EI (Cr) < EI (Co) < EI (Zn) < EI (Ge) (in the same period)

   EI (Ge) < EI (C) (in the same column)

b. Atomic radius:

   ra (Ge) < ra (Zn) < ra (Co) < ra (Cr) < ra (V) (in the same period)

   ra (C) < ra (Ge) (in the same column)

c. Electronegativity:

   V < Cr < Co < Zn < Ge (in the same period)

   Ge < C (in the same column).

Corrected Exercises

Exercise 1:

We consider the following atoms and ions:

$_{17}Cl$, $_{19}K$, $_{20}Ca$, $_{26}Fe$, $_{28}Ni$, $_{42}Mo$, Fe^{3+}, Cl^{-}.

a. Give the electronic configuration of the atoms and ions.

b. Locate these elements in the periodic table (indicate the period and the group).

c. Identify the block of each atom.

d. To which family do these atoms belong?

Exercise 2:

Consider the following elements: $_{56}Ba$, $_{40}Zr$, $_{38}Sr$, $_{31}Ga$, $_{28}Ni$, and $_{24}Cr$.

1. For each element, provide its period, group, and subgroup.
2. Assign to each element the value of its atomic radius from the following options: r (Å): 1.21, 1.25, 2.15, 1.60, and 2.17. Justify your choice.
3. Rank these elements in increasing order of electronegativity.

Exercise 3:

Let the following elements be given: A, B, $_{30}Zn$, $_{25}Mn$.

1. Determine the atomic numbers of elements A and B, knowing that:A belongs to the same period as Zinc (Zn) and to group I_A of the periodic table. B belongs to the same period as Manganese (Mn) and to group VII_A of the periodic table.
2. Provide the stable ions that can be formed by elements A, B, and Mn.
3. To which chemical family do these elements belong?
4. Among these elements, which one has the largest atomic radius and the highest ionization energy? Justify your answer.

Exercise 4:

An element has fewer than 18 electrons and two unpaired electrons. What are its possible configurations?

What is this element if it belongs to the family of antimony ($_{49}Sb$) and the period of sodium ($_{11}Na$)?

Exercise 5:

Consider an element that belongs to the 4th period and has two unpaired electrons.

a. What are the possible configurations?

b. This element is not a transition metal. How many possibilities remain?

c. This element has the smallest atomic radius. What is its electronic configuration?

Exercise 6:

Three elements from the 4th period have, in their ground state, 3 unpaired electrons.

1. Identify these three elements, provide their electronic configurations, and determine their atomic numbers.
2. Specify the position of these elements in the periodic table (group, subgroup, and block).
3. Which of these three elements has the smallest atomic radius? Justify your answer.
4. In the form of a table, give the values of the four quantum numbers {n, ℓ, m, s} characterizing each unpaired electron of the most electronegative element.

Exercise 7:

Find the electronic configuration of the following elements and provide the possible ions they can form:

a. The 6th transition element.
b. A halogen from the 5th period.
c. A noble gas from the same period as $_{34}Se$.

Exercise 8:

Determine the atomic numbers of elements X and Y, knowing that:

- X^{2+}: Has the structure of the noble gas in the fourth period.
- Y^{3-}: Has the structure of the noble gas in the third period.

Exercise 9:

Let the elements be $_{(4x/3)}A$, $_{(2x/3)}B$, $_{(x/2)}C$, and $_{Z}D$. Knowing that:

- Element B belongs to the same period as $_{11}Na$ and the same group as $_{34}Se$.
- D is a transition metal with one unpaired electron characterized by the quantum numbers: (42-2½).

a. Determine the atomic number of these elements and classify them in the periodic table. Represent the valence shell as quantum boxes.

b. Provide the stable ions for each element.

Exercise 10:

The first and second ionization energies of sodium (11Na) and magnesium (12Mg) are as follows (in kJ/mol):

	$_{11}Na$	$_{12}Mg$
1st ionization	496	738
2nd ionization	4562	1451

It is observed that sodium has the lowest first ionization energy and the highest second ionization energy. How can this be explained?

Correction

Exercise 1:

Element	Electronic configuration	Period	Group	Block	Family
$_{17}$Cl	$1s^2\,2s^2\,2p^6\,3s^2\,3p^5$	3	VII$_A$	P	Halogen
$_{19}$K	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$	4	I$_A$	S	Alkali
$_{20}$Ca	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$	4	II$_A$	S	Alkaline earth
$_{26}$Fe	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$	4	VIII$_B$	d	T.M
$_{28}$Ni	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^8$	4	VIII$_B$	d	T.M
$_{42}$Mo	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^4$ $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^1\,4d^5$	5	VI$_B$	d	T.M
Fe^{3+}	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^0 3d^5$				
Cl^-	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$				

T.M: Transition metals

Exercise 2:

1. Period, Group, and Subgroup:

Element	**Electronic Configuration**	**Period**	**Group**
$_{56}$Ba	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^2$	6	II$_A$
$_{40}$Zr	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2$	5	IV$_A$
$_{38}$Sr	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$	5	II$_A$
$_{31}$Ga	$1s^22s^22p^63s^23p^64s^23d^{10}4p^1$	4	II$_A$
$_{24}$Cr	$1s^22s^22p^63s^23p^64s^23d^4$ $1s^22s^22p^63s^23p^64s^13d^5$	4	VI$_B$

2. Assigning Atomic Radius:

The atomic radius generally increases down a group and decreases across a period due to increasing nuclear charge. Using the available radii (in Å), we assign values as follows:

Element	**Atomic radius (Å)**	**Period**	**Group**	**Justification**
$_{56}$Ba	2.17	6	II$_A$	Barium is in Period 6, (largest radius).
$_{38}$Sr	2.15	5	IV$_A$	Strontium is in Period 5.
$_{40}$Zr	1.6	5	II$_A$	Zirconium is in Period 5, (smaller radius than Sr).
$_{31}$Ga	1.21	4	II$_A$	Gallium is in Period 4, (smaller radius).
$_{24}$Cr	1.25	4	VI$_B$	Chromium is in Period 4.

3. Electronegativity Order:

Electronegativity generally increases across a period and decreases down a group.

$EN_{Ba} < EN_{Sr} < EN_{Zr} < EN_{Cr} < EN_{Ga}$.

Exercise 3:

1. Determine the atomic numbers of elements A and B:

A belongs to the period of Zn ($_{30}Zn$: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}$), which is the **4th period**, and to group I_A:

A: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1$ Z=19.

B belongs to the period of Mn ($_{25}Mn$: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^5$, which is the **4th period**, and to group VII_A,

B: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^5$, Z=35.

2. The stable ions that can be formed by elements A, B, and Mn:

$A \longrightarrow A^+$ (Structure of noble gases.).

$B \longrightarrow B^-$ (Structure of noble gases.).

$Mn \longrightarrow Mn^{2+}$ (Very stable d subshell).

3. The chemical family do these elements

A ⟶ Alkali (ns^1)

B ⟶ Halogen ($ns^2\, np^5$)

Mn and Zn ⟶ Transition metals.

4. The element with the largest atomic radius and the highest ionization energy

The four elements belong to the same row (period) n = 4, so we can rank them according to the period: as Z increases, the r decreases, and the Ei increases.

$\underset{\longrightarrow}{Z\nearrow\ r\searrow\ Ei\nearrow\ E_N\nearrow}$

So: $r_B < r_{Zn} < r_{Mn} < r_A$ and $Ei_B > Ei_{Zn} > Ei_{Mn} > Ei_A$

The element with the largest atomic radius is A, and the element with the highest ionization energy is B.

Exercise 4:

a. The possible configurations are:

$1s^2\, 2s^2\, 2p^2$

$1s^2\, 2s^2\, 2p^4$

$1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^2$

$1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^4$

b. Identify the element:

$_{11}Na$: $1s^2\,2s^2\,2p^6\,3s^1$ (3th period)

$_{51}Sb$: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^3$ (Group V_A).

So: X: $1s^22s^22p^63s^23p^3$ (Z=15 and the element is the phosphorus ($_{15}P$).

Exercise 5:

a. In the 4th period, we find the following subshells: 4s, 3d, 4p. The electron configurations that result in two unpaired electrons are as follows:

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^2$

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^8$

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

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

b. This element is not a transition element, so we eliminate the configurations that only contain 4s and 3d in the valence shell, leaving us with only two configurations:

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

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

c. This element has the smallest atomic radius, meaning the largest Z, and therefore the configuration assigned to this element is as follows:

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^4$ (Z=34).

Exercise 6:

1. Identify the three elements with 3 unpaired electrons in the 4th period:

1st: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^3$ (Z=23)

2nd: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^7$ (Z=27).

3th $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}4p^3$ (Z=33).

2. Position of these elements in the periodic table:

1st: Period 4 and group V_B

2nd: Period 4 and group $VIII_B$

3th: Period 4 and group V_A.

3. Smallest atomic radius among these elements:

The elements belong to the same period (n = 4), so we can rank them according to the period:

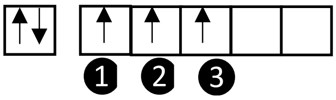
$$\underrightarrow{\underline{Z\nearrow\ \ r\searrow\ Ei\nearrow\ E_N\nearrow}}$$

So, the element with the smallest atomic radius is the third element (Z=33).

4. **Quantum numbers for unpaired electrons of the most electronegative element:**

The most electronegative element among these three is the first (Z=23).

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,/4s^2\,3d^3$



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

Exercise 7:

a. The 6th transition element: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$ (The most stable ion: X^{3+})

b. A halogen from the 5th period: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^5$ (The most stable ion: X^-)

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

${}_{34}$Se: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^4$ (4th period)

So, the electronic configuration is: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6$

Exercise 8:

X^{2+} has the structure of the noble gas of the 4th period ($4s^2\,4p^6$), so X ends with $5s^2$, and the electron configuration of X is:

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2$, $Z = 38$.

Do not forget to fill the 3d subshell between 4s and 4p according to the Aufbau principle.

Y^{3-} has the structure of the noble gas of the 3rd period ($3s^2\,3p^6$), so Y ends with $3s^2\,3p^3$, and the electron configuration of Y is:

$1s^2\,2s^2\,2p^6\,3s^2\,3p^3$, $Z = 15$.

Exercise 9:

Let the elements be ${}_{(4x/3)}A$, ${}_{(2x/3)}B$, ${}_{(x/2)}C$, and ${}_{Z}D$. Knowing that:

- Element B belongs to the same period as ${}_{11}$Na and the same group as ${}_{34}$Se.
- D is a transition metal with one unpaired electron characterized by the quantum numbers: (42-2½).

a. Determine the atomic number of these elements and classify them in the periodic table. Represent the valence shell as quantum boxes.

b. Provide the stable ions for each element.

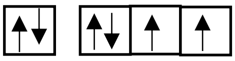
a. Determine the atomic numbers and classify in the periodic table:

${}_{11}$Na: $1s^2\,2s^2\,2p^6\,3s^1$ (Period 3 and group I_A)

$_{34}$Se: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$ (Period 4 and group VI$_A$)

B belongs to the 4th period and to group VI$_A$

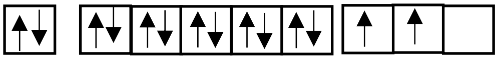
So, B: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ (Z=16).



$_{16}B = _{(2x/3)}B \Longrightarrow \frac{2x}{3} = 16 \Longrightarrow x = 24$

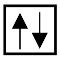
$_{(4x/3)}A = _{32}A \Longrightarrow$ (Z=32).

$_{32}$A: : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$ (Period 4 and group IV$_A$)



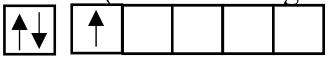
$_{(x/2)}C = _{12}C\ 1s^2 \Longrightarrow$ (Z=12)

$_{12}$C: $1s^2\ 2s^2\ 2p^6\ 3s^2$ (Period 3 and group II$_A$)



D: the quantum numbers (42-2½) describe an electron in a $4d^1$, and D is a transition metal:

D: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^1$ (Period 5 and group III$_B$). (Z=39).



b. Stable ions for each element:

$A \longrightarrow A^{+4}$

$B \longrightarrow B^{-2}$

$C \longrightarrow C^{+2}$

$D \longrightarrow D^{+3}$

Exercise 10 :

The sodium (Na) has the lowest first ionization energy but the highest second ionization energy can be explained by considering the electron configurations and the effects of removing electrons from these elements.

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

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

The first ionization energy refers to the energy required to remove one electron from an atom in its gaseous state. For both sodium and magnesium:

- **Sodium (Na)** has a first ionization energy of 496 kJ/mol. This is relatively low because the single electron in the 3s orbital is far from the nucleus and is shielded by the inner electrons. It's easy to remove this electron.
- **Magnesium (Mg)** has a first ionization energy of 738 kJ/mol**.** Magnesium has two electrons in the 3s orbital, and while the outer electrons are still somewhat shielded, it

takes more energy to remove the first electron than it does for sodium, due to the additional proton in magnesium's nucleus, which exerts a stronger pull on its electrons.

The **second ionization energy** is the energy required to remove a second electron after the first one has been removed:

- **Sodium**: After the first electron is removed, sodium becomes a stable **Na^+ ion** with the configuration, $1s^2$ $2s^2$ $2p^6$ which is a **noble gas configuration**. Removing a second electron would break this stability, making the second electron extremely hard to remove.
- **Magnesium**: After the first electron is removed, magnesium becomes a **Mg^+ ion** with the configuration $1s^2$ $2s^2$ $2p^6$ $3s^1$. The second electron is still in the 3s orbital and not part of a fully stable noble gas configuration, so while it requires more energy to remove than the first, the increase in ionization energy is not as large as sodium’s.

Chapter VI: Chemical Bonds

1. Introduction

Except for inert gases (the last column of the periodic table), which are monatomic, all atoms engage in chemical bonds, forming molecules and/or solids or liquids.

Moreover, even the inert "gases" eventually condense at very low temperatures (or under high pressure). To classify bonds, the two essential concepts are bond energies (or their opposites: dissociation energies) and the electronegativities of the bonded atoms. There are two types of bonds: strong bonds and weak bonds.

2. Strong Bonds

To break strong bonds, it is necessary to provide dissociation energies on the order of 200 to 500 kJ per mole of diatomic bond (approximately 50 to 100 kcal per mole or about 2 to 5 eV per bond).

Four distinct types of strong bonds are distinguished:

- Covalent Bond: Lewis Representation.
- Ionic Bond.
- Iono-covalent Bond. Electric dipole moment.
- Metallic Bond

2.1. Covalent Bond

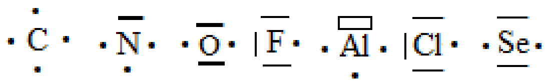
2.1.1. Definition

When two atoms come into contact, they can share their valence electrons and thus form a bond. Each of the two atoms contributes one of its unpaired electrons from the valence shell, each occupying a quantum box (i.e., a single electron). These two electrons pair up to form a bond between atoms A and B. The covalent bond is a strong σ-type bond.

a. Lewis Notations:

The valence electrons of a chemical element are represented by dots distributed around the symbol.

Example:

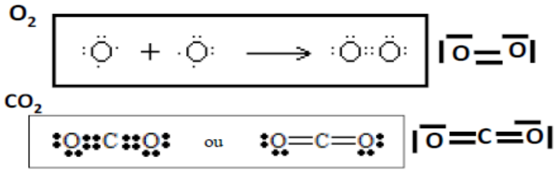


Example: According to the Lewis Representation, HF is represented as follows:

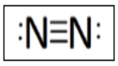
The fluorine atom has 7 peripheral electrons. It shares 1 electron with hydrogen to form a covalent bond.

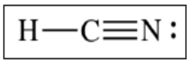
Consequently, it is surrounded by 7+1=8 peripheral electrons. While H_2 has no free electron pairs, fluorine has three in HF (formed by the 6 electrons not involved in the bond).

Example of double bonds: O_2 and CO_2:



Example of triple bonds: N_2 and HCN:





b. Rule of the Octet:

In a molecule, each atom tends to surround itself with eight electrons, except for the hydrogen molecule.

2.1.2. Types of Covalent Bonds

In a covalent bond, each of the two bonded atoms shares one or more electrons from its outermost electron shells; three types of covalent bonds are distinguished.

a. Nonpolar Covalent Bond

If the electronegativity difference between the two atoms is zero or less than 0.4.

Example:

According to the Lewis Representation, H_2 is represented as :

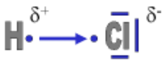
H:H or H−H.

Each hydrogen atom contributes one electron, shared with the other atom to form a bonding pair. Each hydrogen atom is thus surrounded by 1+1=2 valence electrons.

b. Polar Covalent Bond

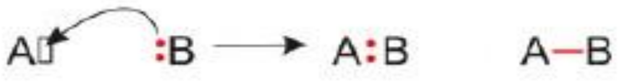
A covalent bond is polar if the electronegativity difference between the two atoms forming the bond is not zero. The more electronegative atom in a polar bond tends to attract the electrons of the covalent bond towards itself.

Example:

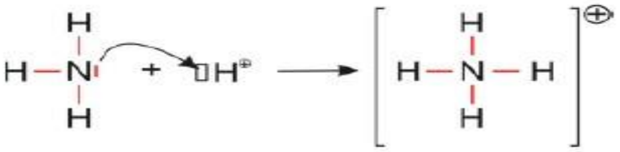


c. Dative Covalent Bond

It forms between two atoms where one of the atoms (atom B) (the donor) provides a lone pair from its outer shell, and the other atom (atom A) (the acceptor), which has an electron deficiency (empty box) in its valence shell (rectangle), receives this lone pair.

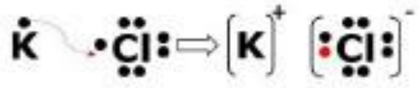


Example: Formation of the ammonium ion NH_4^+



2.2. Ionic Bond

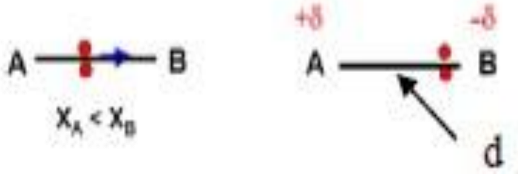
This bond forms between two atoms, A and B, with a significant difference in electronegativity. This difference leads to the transfer of electrons from the less electronegative atom to the more electronegative atom, resulting in the formation of a cation (carrying a positive charge) and an anion (carrying a negative charge).



2.2.1. Dipole Moment

A heteronuclear molecule (AB) is considered an electric dipole if the difference in electronegativity between the two atoms creates polarization.

It results in a negatively charged pole rich in electrons and a positively charged pole lacking electrons at a distance (d) from each other.



This dipole is characterized by its dipole moment or electric moment (μ_{AB}). This quantity (μ_{AB}) is represented by a vector oriented from the negative charge (more electronegative element) to the positive charge (less electronegative element). μ_{AB} is related to the internuclear distance (d) by the following relationship: $\boldsymbol{\mu_{AB} = q\, d_{A\text{-}B}}$

Where:

d is the length of the A-B bond, δ is the partial charge.

The effective partial charges are: $+q=+\delta\cdot e$ and $-q=-\delta\cdot e$, where:

d is the length of the A-B bond,

δ is the partial charge,

e is the elementary charge.

$$\mu_{AB} = |\delta|\cdot e\, d_{A\text{-}B}$$

In the International System of Units, μAB is expressed in Coulomb-meters (C·m). However, the most convenient unit for expressing the dipole moment is the Debye (D):

1 D=3.33×10^{-30} C.m.

For the case of a 100% ionic molecule: **μ_{AB}= e. d**

With e representing the charge of an electron (1.6×10^{-19} C), for the case of a polarized polyatomic molecule, the overall dipole moment of the molecule is the geometric sum of the dipole moments of the individual bonds in the molecule.

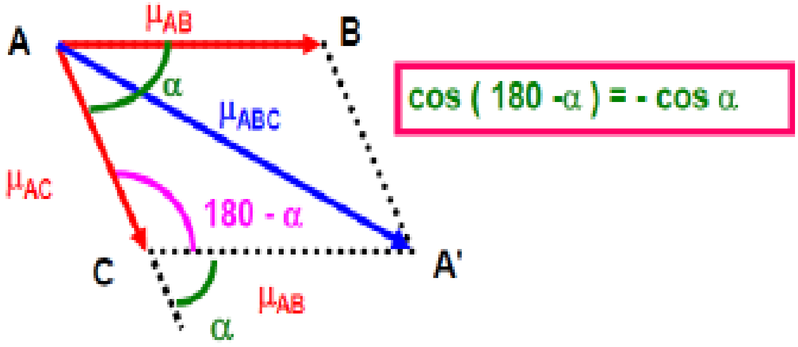


Figure VI.1: Vector representation of the dipole moment of a polyatomic atom ABC.

Generalized Pythagorean theorem in triangle ACA':

Where:

$$\mu_{ABC}^2 = \sum_i \mu_i = \mu_{AB}^2 + \mu_{AC}^2 + 2\,\mu_{AB}\mu_{AC}\cos\alpha$$

μ_i is the dipole moment of each bond i, and α is the angle formed between the two bonds.

In the case where two bonds are identical, the global dipole moment of the molecule is given by:

$$\mu_{ABC}^2 = 2\,\mu\,(1 + \cos\alpha)$$

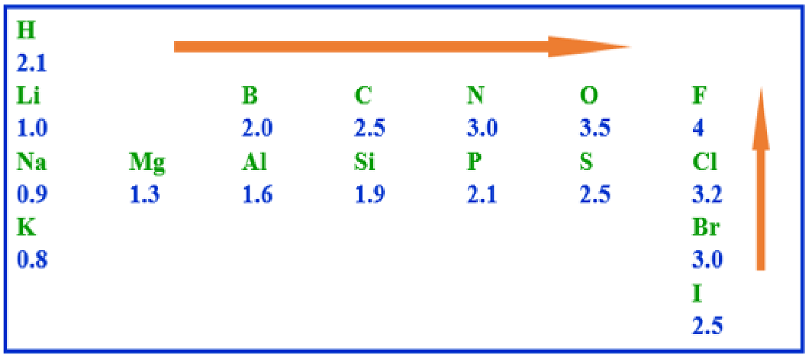
By convention, we can determine the nature of the bond through a simple calculation of the electronegativity difference between the atoms forming that bond.

$\Delta\chi$: Electronegativity difference $(|\Delta\chi=|\chi_2-\chi_1|)$

$\Delta\chi\leq0.4$ ➔ Nonpolar covalent bond

$0.4<\Delta\chi<1.7$ ➔ Polar covalent bond

$\Delta\chi\geq1.7$ ➔ Ionic bond



H 2.1						
Li 1.0		B 2.0	C 2.5	N 3.0	O 3.5	F 4
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.1	S 2.5	Cl 3.2
K 0.8						Br 3.0
						I 2.5

Figure VI.2: Electronegativity values of some important elements.

2.2.2. Partial Ionic Character of the Bond

The partial ionic character of a polar covalent bond can be expressed by the following equation:

$$\%\ ionic\ (A-B) = 100\ \frac{\mu_{AB}\ (experimental)}{\mu_{AB}\ (theor)} = 100\ \frac{\delta.d}{e.d}$$

If the polyatomic molecule (ABC) has a zero-dipole moment, the molecule is linear and nonpolar. On the other hand, if a molecule (ABC) has a nonzero dipole moment, then the molecule is not linear (V-shape) and is polar.

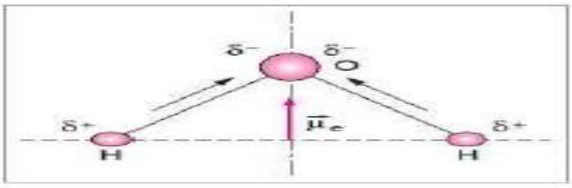


Figure VI.3: The H_2O molecule.

The two arrows along the bonds represent the two components of the electric dipole moment.

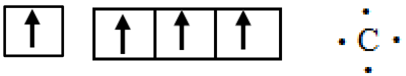
Exercise:

Represent using Lewis diagrams for the following molecules and molecular ions: HCN, $HClO_4$. The HF molecule has a dipole moment (μ) of 1.83 Debye and a bond length (d) of 0.92 Å. Calculate the ionic percentage of this bond.

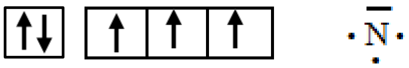
Solution:

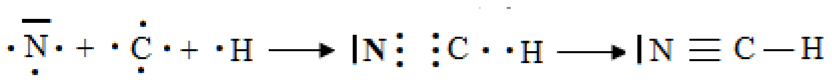
HCN

$_6C^*$: [He] $2s^1$ $2p^3$

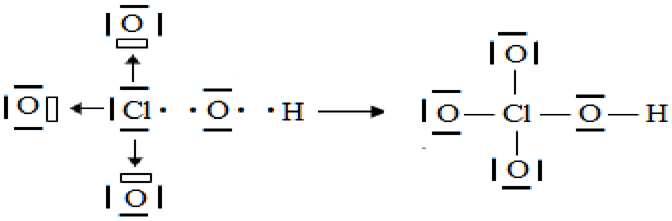


$_7N$: [He] $2s^2$ $2p^3$





$HClO_4$.



Ionic Character Percentage:

$$CI = 100\ \frac{\mu_{AB}\ (experimental)}{\mu_{AB}\ (theor)} \Longrightarrow CI = 100\ \frac{\mu_{AB}\ (experimental)}{e.d}$$

$$CI = 100\ \frac{1.83\ 3.33\ 10^{-30}}{1.6\ 10^{-19}\ 0.82\ 10^{-10}} \Longrightarrow CI = 41.35\%$$

2.3 Metallic Bond

The metallic bond occurs between atoms with low electronegativity that have few electrons in their outer shell. However, it can only form if there is a sufficiently large number of such atoms. That's why it is rarely observed except in certain solids or liquids. Like the ionic bond, it is not a directed bond.

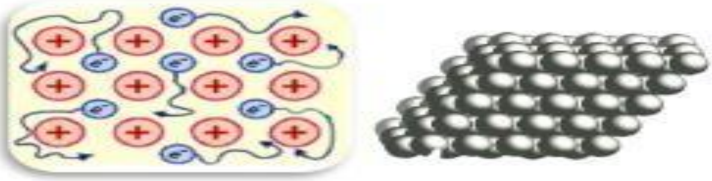


Figure VI.4: Metallic Bond.

3. Weak Bonds

Weak bonds have dissociation energies ranging from about 1 to 40 $kJ\cdot mol^{-1}$, in any case, less than 50 $kJ\cdot mol^{-1}$.

These bonds result from cohesive forces between atoms incapable of forming valence bonds or between molecules where the possibilities of strong bonds are already saturated.

There are two types of weak bonds: Hydrogen bond and van der Waals bonds.

4. Molecular Geometry: Gillespie's Theory or VSEPR

The geometry of a molecule is determined by defining the relative position of the molecule in space.

These relative positions depend on two parameters: Distances between atoms, which are the lengths of the bonds. Angles between atoms forming the molecule.

It allows for the straightforward prediction of the geometric shape of molecules based on the Lewis structure.

VSEPR stands for Valence Shell Electron Pair Repulsion, which means repulsion of electron pairs in the valence shell.

The notation is as follows: AX_mE_n

A: The central atom.

X: Any atom bonded to A (m: number of bonds).

E: Any non-bonding electron pair (NEP) on the central atom A (n: number of N EPs).

The sum (n+m), called the total number of electrons pairs, provides information about the basic geometry of the molecule.

Thus, depending on (n+m), the geometry of the molecule can be predicted: (n+m) =2: Linear shape, =180°α=180°.

(n+m) =3: Triangular shape, =120°α=120°.

(n+m) =4: Tetrahedral shape, =109.5°α=109.5°.

(n+m) =5: Trigonal bipyramidal shape, =90°α=90° and 120°120°. (n+m)=6: Octahedral shape, =180°α=180°.

Table VI.1: Different Possible Shapes Using the VSEPR Theory

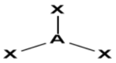
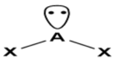
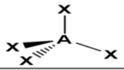
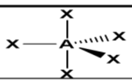
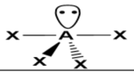
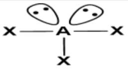
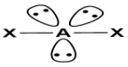
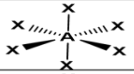
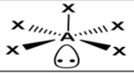
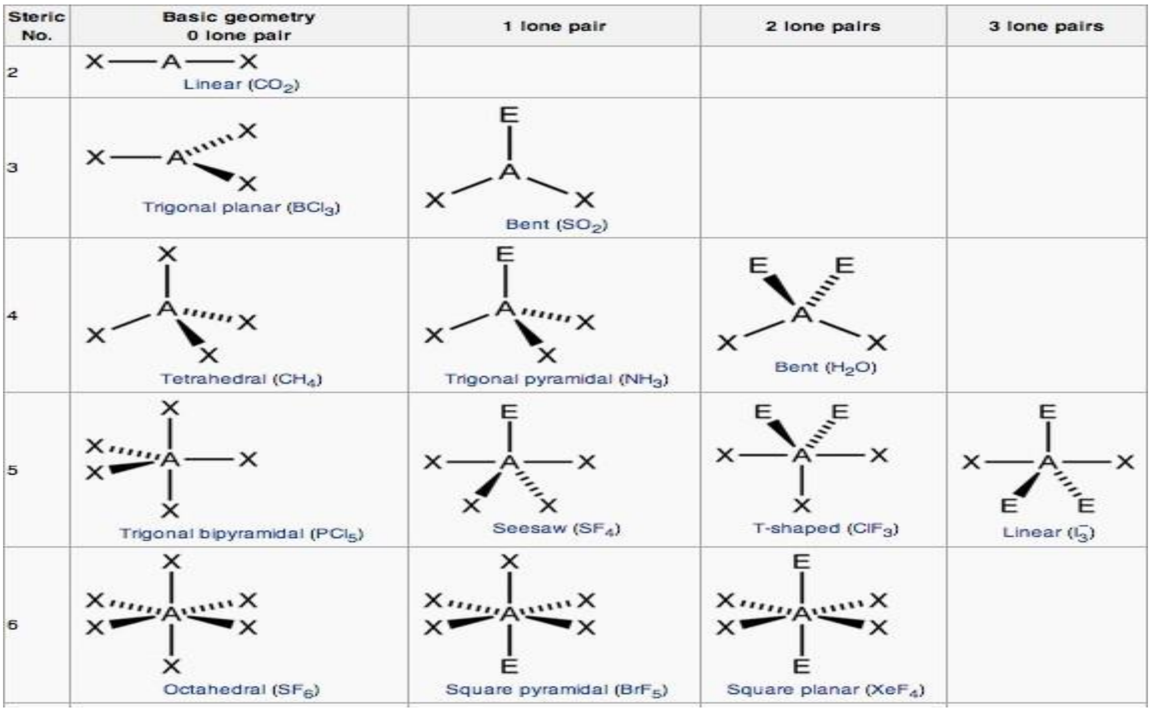
AXE Formula	Molecular Geometry	Bond Angle	Molecule Shape
AX_2E_0	**Linear**	180°	
AX_3E_0	**Trigonal planar**	120°	
AX_2E_1	Bent	119°	
AX_4E_0	**Tetrahedral**	109.5°	
AX_3E_1	Trigonal pyramidal	107.3°	
AX_2E_2	Bent	104.5°	
AX_5E_0	**Trigonal bipyramidal**	90°, 120°, 190°	
AX_4E_1	See-saw	86.5°,102°, 187°	
AX_3E_2	T-shape	87.5°, 185°	
AX_2E_3	Linear	180°	
AX_6E_0	**Octahedral**	90°	
AX_5E_1	Square pyramidal	84.8°, 180°	

Table VI.2: Molecular Geometry (basing on pairs)



Steric No.	Basic geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
2	Linear (CO_2)			
3	Trigonal planar (BCl_3)	Bent (SO_2)		
4	Tetrahedral (CH_4)	Trigonal pyramidal (NH_3)	Bent (H_2O)	
5	Trigonal bipyramidal (PCl_5)	Seesaw (SF_4)	T-shaped (ClF_3)	Linear (I_3^-)
6	Octahedral (SF_6)	Square pyramidal (BrF_5)	Square planar (XeF_4)	

Example of application:

MgF_2

Mg (Z = 12): (2 valence electrons).

These 2 electrons form 2 single bonds with 2 fluorine atoms.

No lone pairs on Mg.

Type: AX2 (2 bonds, no lone pairs).

Geometry: **Linear**, angle = 180°.

MgF_2

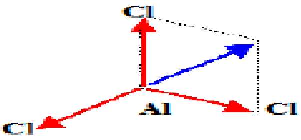
$AlCl_3$

Al (Z = 13) : (3 valence electrons).

These 3 electrons form 3 single bonds with 3 chlorine atoms. No lone pairs on Al.

Type: AX3 (3 bonds, no lone pairs).

Geometry: **Planar triangular**, angle = 120°.



$AlCl_3$

CH_4

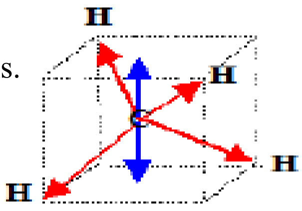
C (Z = 6) : (4 valence electrons).

These 4 electrons form 4 single bonds with 4 hydrogen atoms.

No lone pairs on C.

Type: AX4AX_4AX4 (4 bonds, no lone pairs).

Geometry: **Tetrahedral**, angle = 109.5°.



CH_4

5. Chemical Bonding in the Quantum Model: Hybridization of Atomic Orbitals (AO)

The shortcomings of Lewis theory require the introduction of wave mechanics.

An electron in an atom is described by a wave function $\Phi\Psi = OA$.

An electron in a molecule will be described by a wave function $\Phi = MO$.

Atomic bonding occurs when there is a single electron on an AO that can bond with another single electron belonging to another AO of the same energy or nearby energy, forming a MO with an energy level lower than those of the two AOs.

Let Ha and Hb be two hydrogen atoms.

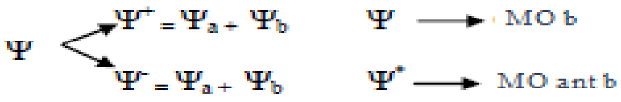
$Ha \rightarrow \Psi a$ (isolated *Ha*) For a bond to occur between Ha and Hb to form the H_2 molecule: $Hb \rightarrow \Psi b$ (isolated *Hb*)

The two atoms must approach each other until a distance r1-2 is reached.

One of the calculation methods used is the L.C.A.O. method (Linear Combination of Atomic Orbitals). If the two atoms bond, there will be a linear combination of the AOs Ψa and Ψb:

$\Psi = a\Psi a + b\Psi b$

The calculations yield a/b = +1 et a/b = -1 (Ha and Hb).



Ψ and Ψ^*, which are actually linear combinations of the AOs Ψa and Ψb, are called molecular orbitals or MOs:

Ψ+ E+ with a bonding energy (E).

Ψ- E+ with an antibonding energy (E*).

The two electrons of the H_2 molecule will have opposite spins and will occupy the lower energy level (the most stable), the bonding MO Ψ+.

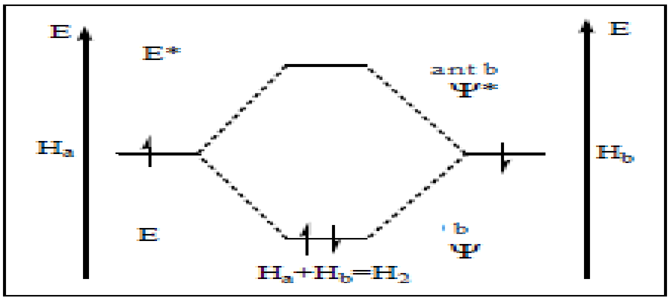
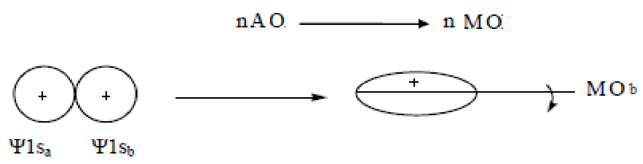


Figure VI.5: Molecular orbital diagram of H_2.

Energy diagram of the H_2 molecule:

By extrapolation: 1 AO or 1 MO can contain a maximum of 2 electrons. 2 AOs combine to give 2 MOs (Ψ, Ψ^*).



Schematic representation of the σ 1s-1s bond in the H_2 molecule:

A covalent bond is formed by the overlap of s-type atomic orbitals.

There is a distribution of charge with cylindrical symmetry, and the overlap is axial (occurs along the axes joining the two nuclei).

The resulting molecular orbital is of the σ type.

Axial overlap: σ bond This is an overlap of two s orbitals, or one s orbital and one p orbital, or even two coaxial p orbitals. The resulting molecular orbitals are called sigma orbitals, and axial overlap gives rise to two sigma MOs (σ, σ*). There is free rotation around the σ bond.

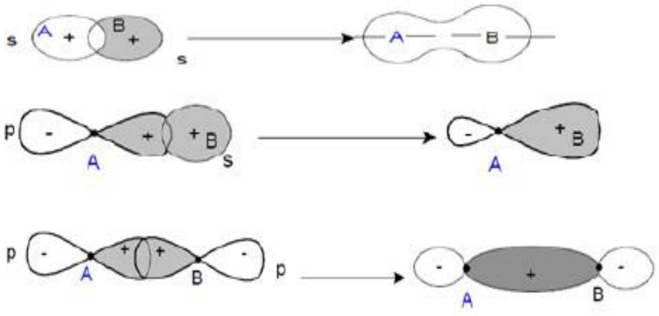


Figure VI.6: Sigma bond and pi bond.

Lateral Overlap: π Bond It involves p orbitals whose axes are parallel. This overlap leads to a π orbital. The corresponding bonds are weaker than σ bonds. In the absence of axial symmetry of the MOs, these bonds do not allow rotation around the bond.

Example:

Molecule HCl

1H : 1s1, 17Cl : [Ne] $3s^2\,3p^5$

During the formation of the H−Cl bond, there is an overlap between the 1s AO of hydrogen and the $3p_z$ AO of chlorine.

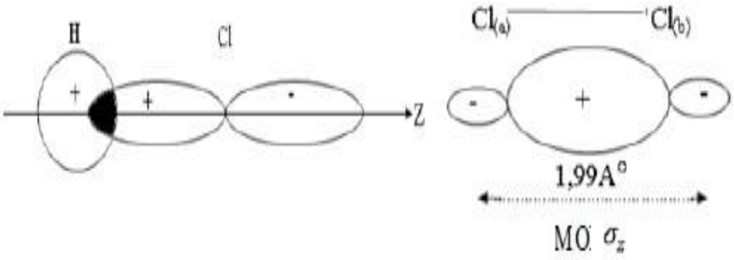


Figure VI.7: Structure of the HCl molecule.

6. Energy Diagram of a Molecule

Similar to atoms, we define an energy diagram (representation of energy levels) for molecules. The filling of MOs follows the rules established for atoms (principle of stability, Pauli principle, and Hund's rule).

Maximum overlap (bonding) occurs between AOs of the same energy or neighboring energies.

We also define the bond order (or index or number):

B.O. or $i=2(n-n^{*})$ where:

- n is the number of bonding electrons (located on a bonding MO).
- $n*$ is the number of antibonding electrons (located on an antibonding MO).

6.1. Homonuclear Molecules

Example:

Oxygen Molecule (O_2)

- Atomic configuration of O atom: $1s^2\ 2s^2\ 2p^4$
- Total electrons in O_2: 16 electrons

Electron Configuration (MO Theory) for O_2:

$(\sigma_{1s})^2\ (\sigma_{1s}^*)^2\ (\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\sigma_{2pz})^2\ (\pi_{2px})^2\ (\pi_{2py})^2\ (\pi_{2px})^1\ (\pi_{2py})^1$

Bond Order (B.O.) Calculation:

Bond Order=12(number of bonding electrons−number of antibonding electrons)

- Bonding electrons:
  $(\sigma_{1s})^2, (\sigma_{2s})^2, (\sigma_{2pz})^2, (\pi_{2px})^2, (\pi_{2py})^2 \rightarrow$ 8 electrons
- Antibonding electrons:
  $(\sigma_{1s}^*)^2, (\sigma_{2s}^*)^2, (\pi_{2px})^1, (\pi_{2py})^1 \rightarrow$ 4 electrons

B.O.=12(8−4)=2→ A double bond

MO Diagram for Homonuclear Diatomic Molecule of Type A_2 (Oxygen):

- Core orbitals: $(\sigma_{1s})^2\ (\sigma_{1s}^*)^2$
  Valence orbitals: $(\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\sigma_{2pz})^2\ (\pi_{2px})^2\ (\pi_{2py})^2\ (\pi_{2px})^1\ (\pi_{2py})^1$

Note:

For molecules with atomic number Z > 7 (like oxygen), the 2p molecular orbitals follow this energy order:

$\sigma(2pz)<\pi(2px),\pi(2py)<\pi*(2px),\pi*(2py)<\sigma*(2pz)$

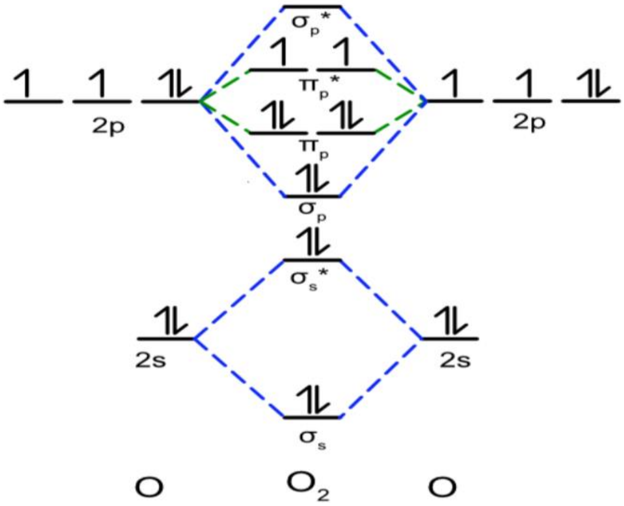


Figure VI.8: MO diagram of O_2.

There is a double bond between the two oxygen atoms (in Lewis notation: O=O), which does not accurately represent reality.

Indeed, on the diagram, there are two lone electrons on the two antibonding orbitals (following Hund's rule), giving this molecule paramagnetic properties.

The explanation of this paramagnetic phenomenon of oxygen was a notable success for the molecular orbital theory.

6.2. Heteronuclear Molecules (*AB*)

Example:

The molecule (HF) / H: $1s^1$ / F: $1s^2 2s^2 2p^5$

Since fluorine is more electronegative than hydrogen, its AOs will be more stable (lower energy) than those of the hydrogen atom.

The AOs that will combine are those with the closest energies (the 1*s* AO of hydrogen and one of the 2*p* AOs of fluorine).

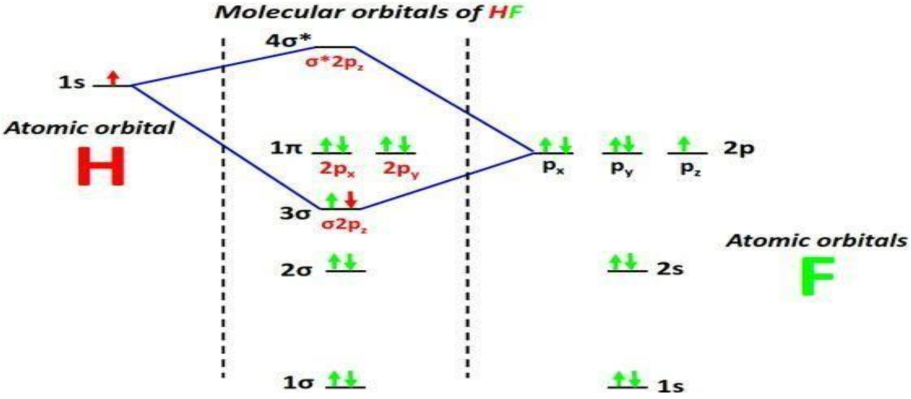


Figure VI.9: MO diagram of HF.

The linear combination of the 1*s* AO of hydrogen and the 2*pz* AO gives rise to two MOs: a bonding MO (σ), with lower energy than the two AOs, and an antibonding MO ($\sigma*$) with higher energy.

The unused 2*s*, $2p_x$, and $2p_y$ AOs will result in MOs with the same energy as these AOs. These are nonbonding MOs localized around the fluorine atom.

A ($\sigma 2p-1s$) bond is formed between F and H.

Calculation: B.O. (i)=1/2($n-n*$)=1/2(2−0)=1.

7. Hybridization of Atomic Orbitals (AOs)

Hybridization is the formation of equivalent hybrid orbitals by linear combination of atomic orbitals (s and p) or (s, p, and d) of the same atom. This phenomenon can occur after electron excitation. Hybridization involves mixing orbitals of an atom to form new hybrid orbitals that better describe qualitatively the bonds between atoms. The resulting hybrid orbitals are very useful in explaining the shape of molecular orbitals in molecules.

7.1. Different Types of Hybridization

7.1.1. SP^3 Hybridization

This is referred to as *sp*3 hybridization of carbon. The 4 sp^3 hybrid orbitals correspond to more stable energy states for valence electrons. They form 4 identical bonds at 109.5°.

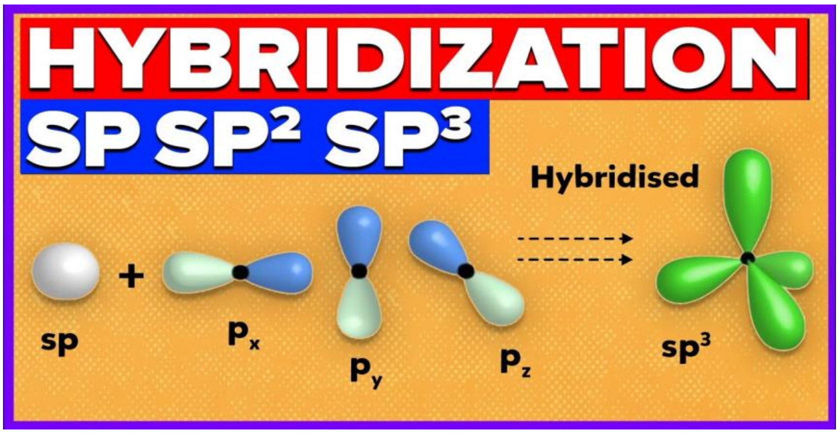


Figure VI.10: SP^3 Hybridization.

S orbitals being spherical and P orbitals pointing along the three Cartesian axes, it is not straightforward to explain the formation of a tetrahedral molecule.

The atomic orbitals involved in its formation are the 2s and 2p orbitals of the carbon atom, which will overlap with the 1s orbitals of hydrogen: $1s+3p \rightarrow 4sp^3$.

sp^3 hybridization explains the spatial configuration of molecules like CH_4.

In the scheme below:

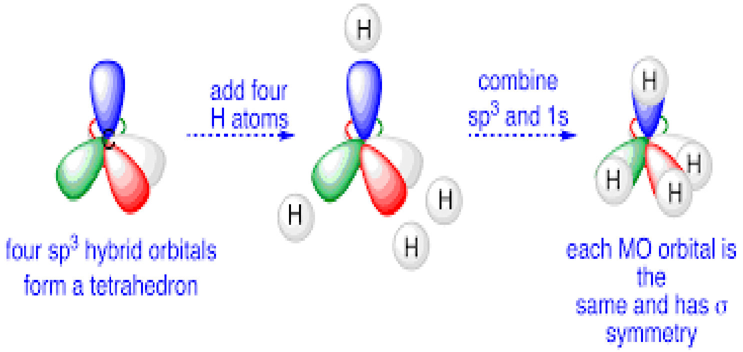


Figure VI.11: SP^3 Hybridization of CH_4.

7.1.2. SP^2 Hybridization

The exponent 2 here indicates that only two p orbitals will be combined with the s orbital to obtain this type of hybrid orbitals.

Thus, there will be one remaining p orbital on each carbon atom: $1s+3p \rightarrow 3sp^2+1p$.

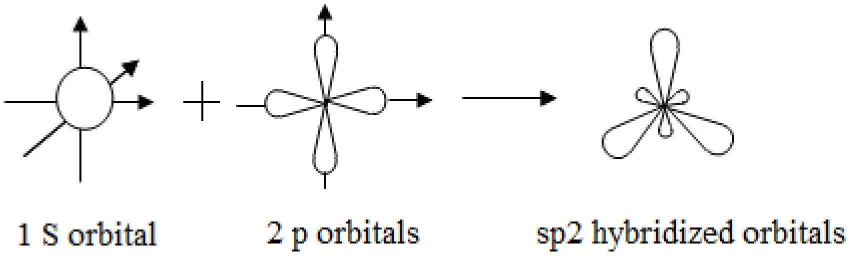


Figure VI.12: SP^2 Hybridization.

These sp^2 hybrid orbitals will point in the directions of an equilateral triangle centered on the carbon atom.

The sp^2 hybridization explains the spatial configuration of molecules such as C_2H_4 with the following diagram:

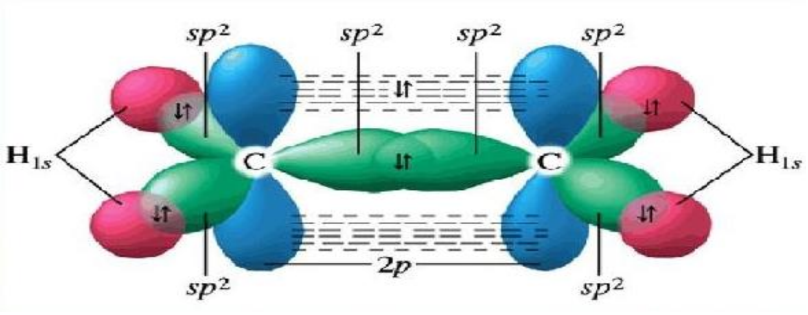


Figure VI.13: SP^2 Hybridization of C_2H_4.

7.1.3. SP Hybridization

To describe the C_2H_2 molecule, we will use hybrid atomic orbitals obtained by a linear combination of the 2s atomic orbital and only one of the 2p atomic orbitals. This results in 2 sp hybrid atomic orbitals and 2 remaining pure 2p atomic orbitals.

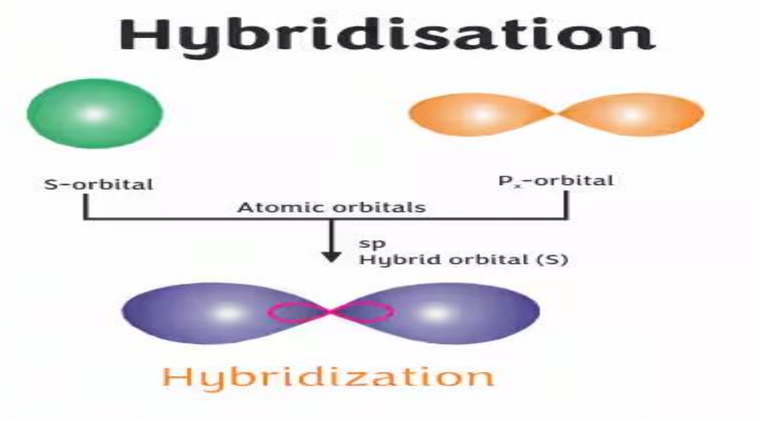


Figure VI.14: SP Hybridization.

These hybrid orbitals are denoted as sp and point 180° away from each other. SP hybridization explains the spatial configuration of molecules like acetylene (C_2H_2), which is a linear molecule with two carbons triply bonded, as shown in the following diagram:

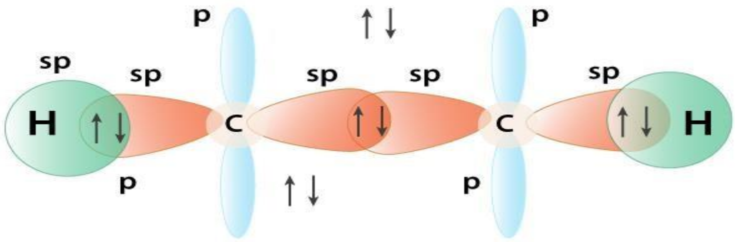


Figure VI.15: SP Hybridization of C_2H_2.

The most common cases of atomic orbital hybridization correspond to the geometric shapes already described in the VSEPR method:

- **Linear:** 180°, Hybridization: sp
- **Trigonal planar:** 120°, Hybridization: sp^2
- **Tetrahedral:** 109.5°, Hybridization: sp^3
- **Trigonal bipyramidal:** 3x120°, Hybridization: sp^3d (dp + sp^2)
- **Octahedral:** 6x90°, Hybridization: sp^3d^2

Application:

The molecule CCl_4 is nonpolar. What can be deduced about its geometric shape?

What is the hybridization state of the carbon atom in this compound?

Solution:

Since CCl_4 is nonpolar, the chlorine atoms are arranged symmetrically around the central atom (the central atom occupies the centroid of the geometric figure), minimizing the interactions between the chlorine atoms.

The hybridization state of carbon is sp^3; four sp^3 hybridized atomic orbitals form four single bonds with four chlorine atoms, resulting in a tetrahedral shape for CCl_4.

Corrected Exercises

Exercise 1:

1. Provide the Lewis structures for the following molecules and molecular ions:

CH_4, CO_2, HCN, SO_3, ClO^-,NO_2^+. $POCl_3$

2. Indicate the type of bonds in each case.

Data: $_1H$, $_6C$, $_7N$, $_8O$, $_{16}S$, $_{17}Cl$.

Exercise 2:

1- Based on the electronic structures of boron and phosphorus atoms, explain the formation of the following molecules: PCl_3, PCl_5, and BCl_3. Is the octet rule satisfied in these molecules?

2- Determine the valence of phosphorus in the following two molecules: PCl_3 and PCl_5.

Exercise 3:

1- By applying Gillespie's rules or the VSEPR method (Valence Shell Electron Pair Repulsion), predict the AXmEn classification and the geometry of the following compounds: CH_4, $SiCl_4$, $AlCl_3$, HCN, PF_3, H_2S, PCl_5, $XeOF_4$.

2- In the molecules $SiCl_4$, PF_3, and H_2S, the bond angles are respectively 109.5°, 107.3°, and 104.5°. Explain this trend.

Exercise 4:

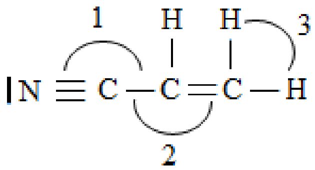
Given the following molecules:

CH_4, NH_3, $AlCl_3$, H_2S, $BeCl_2$, PCl_5, HCN, SF_6,

Determine the hybridization state of the central atom.

Exercise 5:

1- Estimate the bond angles in the following molecules: BF_3, Cl_2CO, SO_2.



2- Estimate the values of angles 1, 2, and 3 in the molecule C_3H_3N.

Exercise 6:

1- Assign the partial charges (δ+ and δ-) and indicate the direction of the dipole moment for the bonds in the following molecules: HF; PCl_3; H_2O; CCl_4.

2- Rank the following bonds in decreasing order of polarity: O-H; C-Cl; H-F; P-Cl; C-O.

Data: Electronegativity values according to Pauling: $_1H$ (2,1); $_6C$ (2,5); $_8O$(3,5); $_9F$ (4,0); $_{15}P$(2,1); $_{17}Cl$ (3,0).

Exercise 7:

Consider the following molecules: $BeCl_2$, CO_2, SO_2, CCl_4, $CHCl_3$, SF_4.

Study the polarity of these molecules.

Exercise 8:

The dipole moment of the hydrogen sulfide (H_2S) molecule is 0.95 Debye, and the dipole moment of the S-H bond is 0.67 D.

1. Calculate the value of the H-S-H bond angle.
2. Calculate the charges carried by the sulfur and hydrogen atoms, given that the S-H bond length is 1.33 Å.
3. Calculate the ionic percentage of the S-H bond.

Exercise 9:

The dipole moment of the Li-H bond is μ = 5.88 Debye, and its partial ionic character is 77%.

1- Determine the partial charges on each of the two atoms.

2- Calculate the bond length of the Li-H bond.

Exercise 10:

1- Provide the molecular orbital (MO) energy diagram and the electronic structure of the NO molecule.

2- Identify the highest energy occupied molecular orbital.

3- Is the NO molecule paramagnetic or diamagnetic?

Data: $_7N$, $_8O$.

Correction

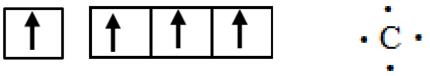
Exercise 1:

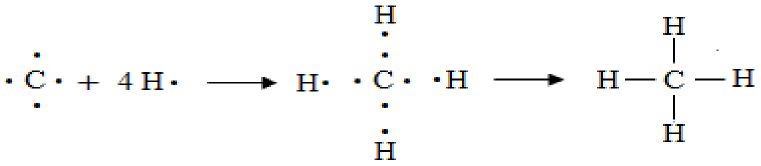
1. The Lewis notation of molecular molecules and ions.

CH4

The central atom is carbon.

$_6C^*$: [He] $2s^1$ $2p^3$



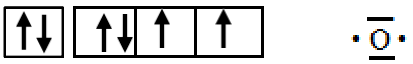


Four single covalent bonds are formed (each atom donates one electron to form the bond).

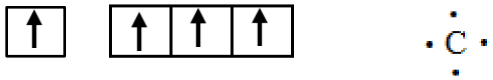
CO_2

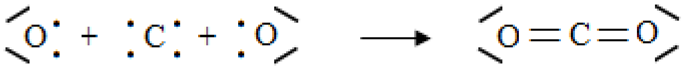
The central atom is carbon.

${}_8O$: [He] $2s^2 2p^4$



${}_6C^*$: [He] $2s^1 2p^3$



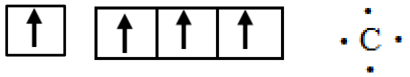


The two bonds formed are double covalent bonds.

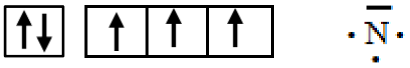
HCN

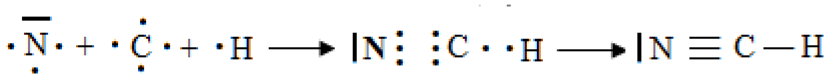
The central atom is carbon.

${}_6C^*$: [He] $2s^1$ $2p^3$



${}_7N$: [He] $2s^2$ $2p^3$



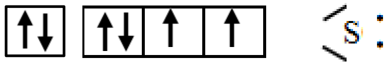


A single covalent bond and a triple covalent bond are formed.

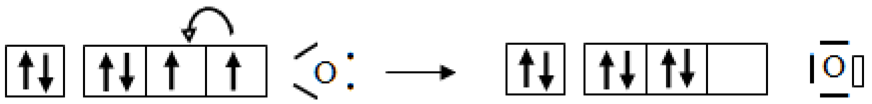
SO_3

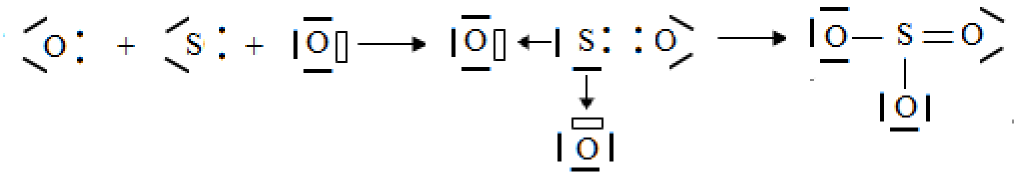
The central atom is sulfur.

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



${}_8O$: $1s^2/2s^2 2p^4$ Rearrangement of oxygen's electrons to create an electron deficiency.



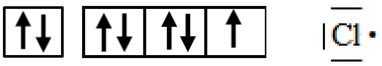


Three bonds are formed: a double covalent bond and two coordinate covalent bonds (the sulfur atom has provided a lone pair to the oxygen atom, which has an empty orbital).

ClO^-

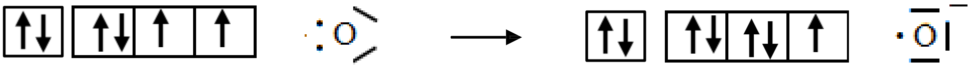
The central atom is chlorine.

$_{17}C: 1s^2/ 2s^2 2p^6/ 3s^2 \quad 3p^5$



The negative charge is carried by the most electronegative atom (oxygen).

$_{8}O: 1s^2/2s^2 \quad 2p^4$ $\qquad$ $_{8}O^-: 1s^2/ 2s^2 \quad 2p^5$

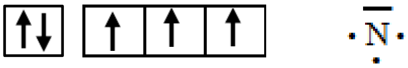


The bond formed is a single covalent bond.

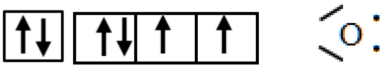
NO_2^+

The central atom is nitrogen.

$_{7}N: 1s^2/ \ 2s^2 \quad 2p^3$

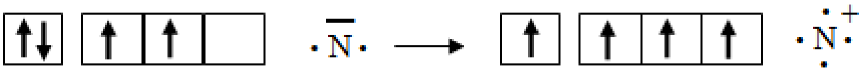


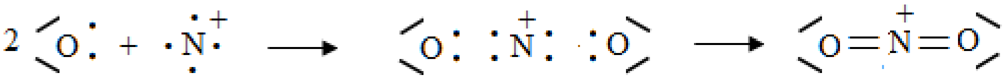
$_{8}O: 1s^2/2s^2 \quad 2p^4$



The positive charge is carried by the most electropositive atom, which is nitrogen.

$_{7}N^+: 1s^2 / 2s^2 \quad 2p^2$ After excitation. $_{7}N^{+*}: 1s^2 / 2s^1 \ 2p^3$



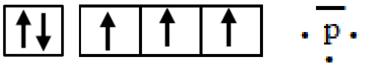


The two bonds formed are double covalent bonds.

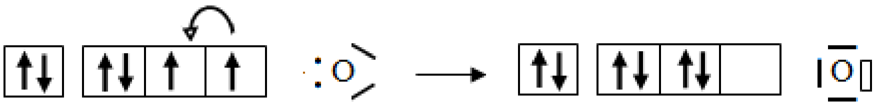
POCl₃

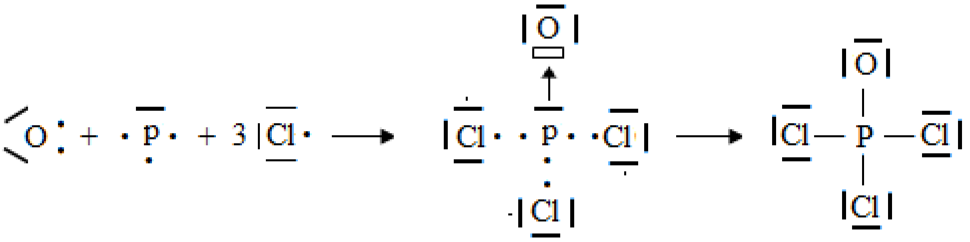
The central atom is phosphorus.

$_{15}P: 1s^2/\ 2s^2 2p^6/\ 3s^2 \quad 3p^3$



$_{8}O: 1s^2/\ 2s^2\ \ 2p^4$ After the rearrangement.





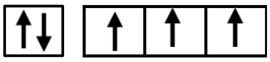
The three bonds formed between the phosphorus atom and the chlorine atoms are single covalent bonds, and the bond between phosphorus and oxygen is a coordinate covalent bond.

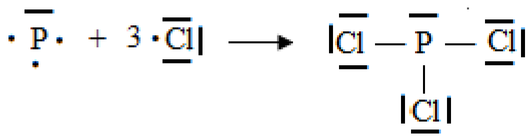
Exercise 2:

1. The octet rule

PCl₃

$_{15}P : 1s^2/\ 2s^2\ 2p^6/\ 3s^2 \quad 3p^3$

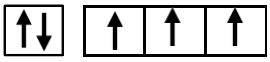




In the PCl3 molecule, all the atoms are surrounded by 4 pairs of electrons. Therefore, this molecule follows the octet rule.

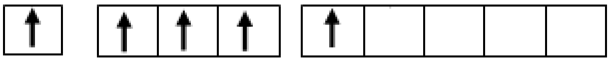
PCl₅

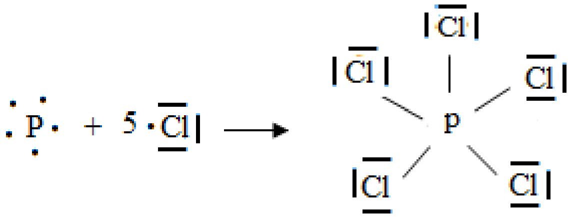
$_{15}P : 1s^2/\ 2s^2\ 2p^6/\ 3s^2 \quad 3p^3$

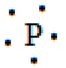


To form this molecule, the phosphorus atom must transition to its excited state.

$_{15}P^* : 1s^2/\ 2s^2\ 2p^6/\ 3s^1 \quad 3p^3 \quad 3d^1$



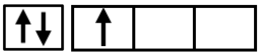




In the PCl_5 molecule, the phosphorus atom is surrounded by 5 pairs of electrons. This molecule does not follow the octet rule due to an excess of electrons.

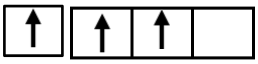
BCl_3

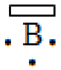
${}_5B$: $1s^2$/ $2s^2 2p^1$

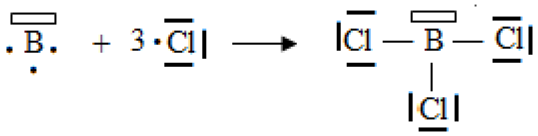


To form this molecule, the boron atom must transition to its excited state.

${}_5B^*$: $1s^2$/ $2s^1$ $2p^2$







In the BCl_3 molecule, the boron atom is surrounded by 3 pairs of electrons. This molecule does not follow the octet rule due to a deficiency of electrons.

2. The valence of phosphorus

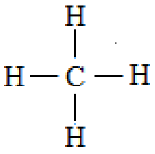
In the PCl_3 molecule, the phosphorus atom has formed 3 bonds, so its valence is 3.

In the PCl_5 molecule, the valence of phosphorus is 5 since it has formed 5 bonds.

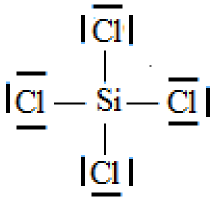
Exercise 3:

1 The group affiliation and geometry of the molecules

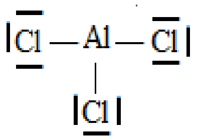
CH_4: In the CH_4 molecule, the central atom, carbon (C), is surrounded by 4 bonding pairs of electrons. The group affiliation is of type AX_4, and the shape of the molecule is tetrahedral.



SiCl$_4$: In the SiCl$_4$ molecule, the central atom, silicon (Si), is surrounded by 4 bonding pairs of electrons. The group affiliation is of type AX$_4$, and the shape of the molecule is tetrahedral.



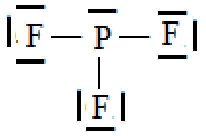
AlCl$_3$: In the AlCl$_3$ molecule, the central atom, aluminum (Al), is surrounded by 3 bonding pairs of electrons. The group affiliation is of type AX$_3$, and the shape of the molecule is trigonal planar.



HCN: In the HCN molecule, the central atom, carbon (C), is surrounded by 2 bonding pairs of electrons (the triple bond is considered as a single bond). The group affiliation is of type AX$_2$, and the shape of the molecule is linear.

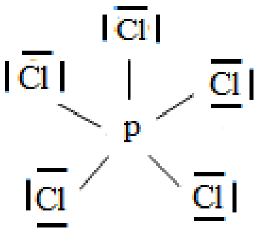
$$|N \equiv C - H$$

PF$_3$: In the PF$_3$ molecule, the central atom, phosphorus (P), is surrounded by 3 bonding pairs of electrons and 1 lone pair. The group affiliation is of type AX$_3$E$_1$, and the shape of the molecule is trigonal pyramidal.

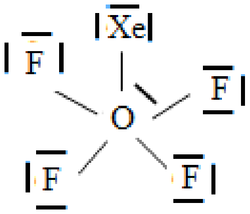


H$_2$S: In the H$_2$S molecule, the central atom, sulfur (S), is surrounded by 2 bonding pairs of electrons and 2 lone pairs. The group affiliation is of type AX$_2$E$_2$, and the shape of the molecule is bent.

PCl$_5$: In the PCl$_5$ molecule, the central atom, phosphorus (P), is surrounded by 5 bonding pairs of electrons. The group affiliation is of type AX$_5$, and the shape of the molecule is trigonal bipyramidal.



$XeOF_4$: In the $XeOF_4$ molecule, the central atom, oxygen (which is less electronegative than xenon), is surrounded by 5 bonding pairs of electrons and 1 lone pair. The group affiliation is of type AX_5E_1, and the shape of the molecule is square pyramidal.



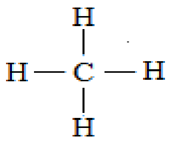
2. The bond angles in the molecules $SiCl4$, $PF3$, and $H2S$.

The central atom in the $SiCl_4$ molecule is surrounded by four bonding pairs of electrons, so its geometry is tetrahedral with a bond angle of 109.5°. In the case of PF_3, the geometry is trigonal pyramidal due to the presence of a lone pair on the phosphorus atom. The three P-F bonds tend to move slightly away from the lone pair and come closer to each other: the bond angle decreases compared to the value observed in $SiCl_4$. The presence of two lone pairs on the sulfur atom in the H_2S molecule forces the two S-H bonds to come even closer: the bond angle is smaller than in PF_3. It should be noted that the repulsion between lone pairs – lone pairs is stronger than lone pair – bonding pair, and is also stronger than bonding pair – bonding pair.

Exercise 4:

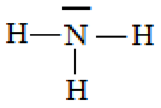
The type of hybridization of an atom is determined by the number of bonding and lone pairs of electrons.

CH_4



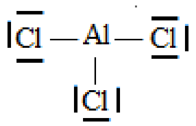
The central atom, carbon (C), is surrounded by 4 bonding pairs of electrons, so there are 4 hybridized atomic orbitals, and the type of hybridization is **sp^3**.

NH_3



The central atom, nitrogen (N), is surrounded by 4 pairs of electrons (3 bonding pairs and 1 lone pair), so there are 4 hybridized atomic orbitals, and the type of hybridization is **sp^3**.

$AlCl_3$

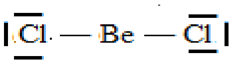


The central atom, aluminum (Al), is surrounded by 3 bonding pairs of electrons, so there are 3 hybridized atomic orbitals, and the type of hybridization is **sp^2**.

H_2S

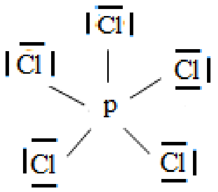
The central atom, sulfur (S), is surrounded by 4 pairs of electrons (2 bonding pairs and 2 lone pairs), so there are 4 hybridized atomic orbitals, and the type of hybridization is **sp^3**.

$BeCl_2$



The central atom, beryllium (Be), is surrounded by 2 bonding pairs of electrons, so there are 2 hybridized atomic orbitals, and the type of hybridization is **sp**.

PCl_5



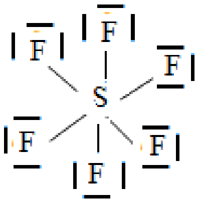
The central atom, phosphorus (P), is surrounded by 5 bonding pairs of electrons, so there are 5 hybridized atomic orbitals, and the type of hybridization is **sp^3d**.

HCN

$|N \equiv C - H$

The central atom, carbon (C), is surrounded by 2 bonding pairs of electrons (the triple bond is considered as a single bond), so there are 2 hybridized atomic orbitals, and the type of hybridization is **sp**.

SF_6

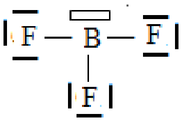


The central atom, sulfur (S), is surrounded by 6 bonding pairs of electrons, so there are 6 hybridized atomic orbitals, and the type of hybridization is **sp^3d^2**.

Exercise 5:

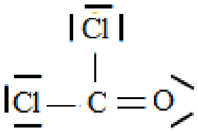
1. The bond angle value in each molecule.

BF3



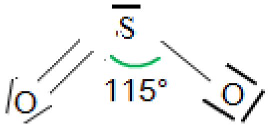
The group affiliation of the molecule is AX_3, so its geometry is trigonal. The bond angle $F\hat{B}F$ value is 120°.

Cl_2CO



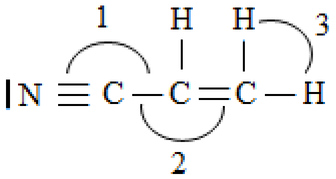
The group affiliation of the molecule is AX_3, so its geometry is trigonal. The bond angles $Cl\hat{C}O$ and $Cl\hat{C}Cl$ are 120°.

SO_2



The group affiliation of this molecule is AX2E1, so its geometry is trigonal with an inverted V shape. The bond angle is less than 120° due to the presence of a lone pair on sulfur (the bond angle $O\hat{S}O$ is 115°).

2. The bond angle values of 1, 2, and 3 in the C3H3N molecule.



Carbon atom 1 is surrounded by 2 bonding pairs of electrons, so the electronic arrangement around this atom is linear, and the bond angle $N\hat{C}C$ is 180°.

Carbon atoms 2 and 3 are surrounded by 3 bonding pairs of electrons, so the geometry is trigonal planar, and the bond angles $C\hat{C}C$ and $H\hat{C}H$ are 120°.

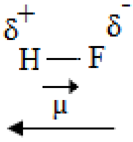
Exercise 6:

Partial charges and the direction of the dipole moment:

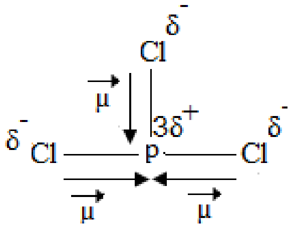
The partial negative charge (δ-) is carried by the most electronegative atom, and the partial positive charge (δ+) is carried by the most electropositive atom.

The direction of the dipole moment is from the negative pole to the positive pole.

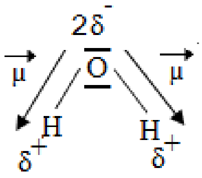
HF



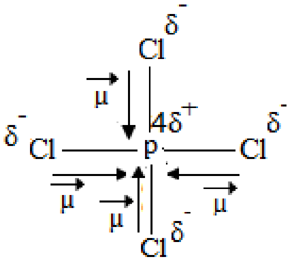
PCl_3



H_2O



PCl_4



2- Ranking in descending order of polarity:

The polarity of a bond is greater when the electronegativity difference is larger.

The Bond	O-H	C-Cl	H-F	P-Cl	C-O
Δ (En)	1.4	0.5	1.9	0.9	1

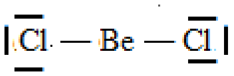
The polarity of the bonds is given in the following order: H-F > O-H > C-O > P-Cl > C-Cl.

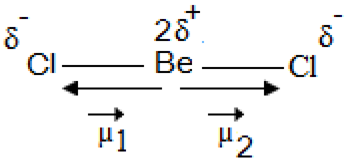
Exercise 7:

In the case of polyatomic molecules, polarity depends on the presence of a polarized bond and the geometry of the molecule.

$BeCl_2$: The molecule is nonpolar

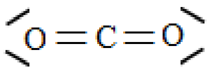
In the $BeCl_2$ molecule, the two Be-Cl bonds are polar and identical. The magnitude of their dipole moment vectors is the same, but they point in opposite directions (linear geometry), so their vector sum is zero. $\vec{\mu} = \vec{\mu}_1 + \vec{\mu}_2 = 0$

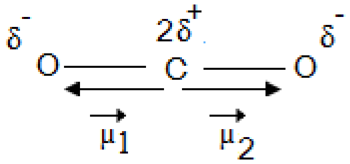




CO_2: The molecule is nonpolar.

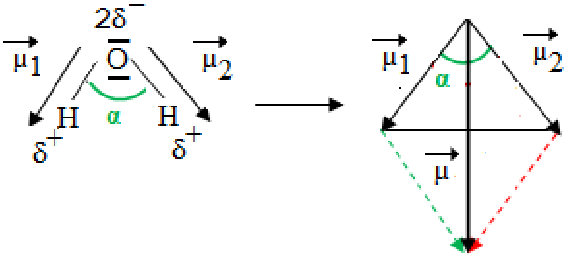
In the CO_2 molecule, the two C-O bonds are polar. The magnitude of their dipole moment vectors is the same, but they point in opposite directions (linear geometry). Therefore, their vector sum is zero. $\vec{\mu} = \vec{\mu}_1 + \vec{\mu}_2 = 0$





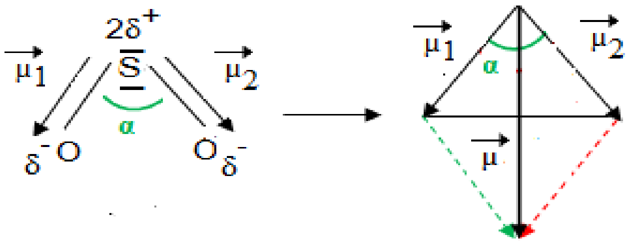
H_2O: The molecule is polar.

In the H_2O molecule, the two O-H bonds are polar. The magnitude of their dipole moment vectors is the same, with a bond angle of 104.5° between the two vectors (bent geometry). Therefore, their vector sum is not zero.



SO_2: The molecule is polar.

In the SO_2 molecule, the two S-O bonds are polar. The geometry is bent (with an angle between the two vectors). Therefore, their vector sum is not zero.

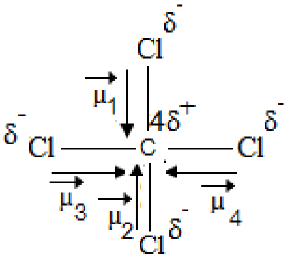


CCl_4: The molecule is nonpolar.

In the CCl_4 molecule, the four C-Cl bonds are polar. The tetrahedral geometry of CCl_4 indicates the presence of symmetry (identical bond angles, identical bond lengths, and the same peripheral atoms). Therefore, the vector sum of the four dipole moments is zero.

$\vec{\mu} = \vec{\mu_1} + \vec{\mu_2} + \vec{\mu_3} + \vec{\mu_4}$

$\vec{\mu_1} + \vec{\mu_2} = 0$ and $\vec{\mu_3} + \vec{\mu_4} = 0$ so $\vec{\mu} = 0$

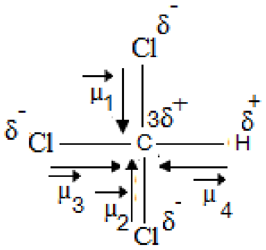


$CHCl_3$: The molecule is polar.

In the $CHCl_3$ molecule, the three C-Cl bonds are polar. The geometry is tetrahedral, as in the case of CCl_4, but the peripheral atoms are different (one Cl atom is replaced by an H atom), which disrupts the symmetry (the bond lengths are different). Therefore, the vector sum of the four dipole moments is not zero.

$\vec{\mu} = \vec{\mu_1} + \vec{\mu_2} + \vec{\mu_3} + \vec{\mu_4}$

$\vec{\mu_1} + \vec{\mu_2} = 0$ and $\vec{\mu_3} + \vec{\mu_4} \neq 0$ so $\vec{\mu} = \vec{\mu_3} + \vec{\mu_4}$

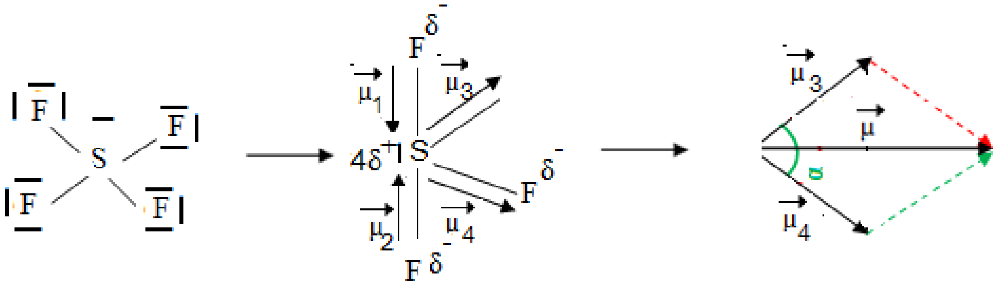


SF_4: The molecule is polar

In the SF_4 molecule, the four S-F bonds are polar. The geometry is a distorted tetrahedron, and the presence of a lone pair on the sulfur atom disrupts the symmetry. Therefore, the vector sum of the four dipole moments is not zero.

$\vec{\mu} = \vec{\mu_1} + \vec{\mu_2} + \vec{\mu_3} + \vec{\mu_4}$

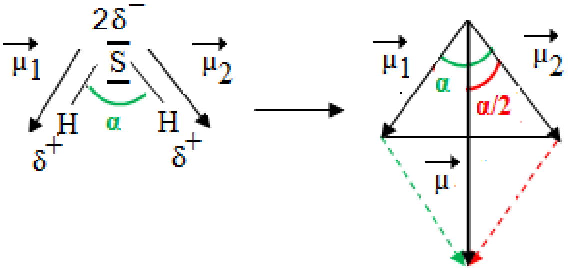
$\vec{\mu_1} + \vec{\mu_2} = 0 \Rightarrow \vec{\mu} = \vec{\mu_3} + \vec{\mu_4}$



Exercise 8:

1. Calculation of the H-S-H angle

The dipole moment of the molecule $\vec{\mu} = \vec{\mu}_1 + \vec{\mu}_2$



$$cos\frac{\alpha}{2} = \frac{\frac{\mu}{2}}{\mu 2} = \frac{\frac{\mu H_2S}{2}}{\mu S - H} = \frac{\frac{0.95}{2}}{0.67} = 0.71 \implies \alpha = 89.53°.$$

2. The partial charge carried by the sulfur (S) atoms and the hydrogen (H) atom.

$$\mu S - H = \delta\, d_{S-H} \implies \delta = \frac{\mu_{S-H}}{d_{S-H}} = \frac{0.67 \text{ x } 3.33 \text{ x } 10^{-30}}{1.33 \,.\, 10^{-10}} = 1.67.\,10^{-20}\, C$$

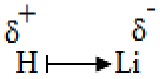
3. The partial ionic percentage

$$\%PIC = \frac{(\mu_{A-B})exp}{(\mu_{A-B})ion} \text{ x } 100 = \frac{\delta\, d}{e\, d} \text{x } 100 = \frac{\delta}{e} \text{ x}100 = \frac{1.67\ 10^{-20}}{1.6\ 10^{-19}} \text{ x } 100 = 10.4\%$$

The S-H bond is 10.44% ionic.

Exercise 9:

1. The partial charges carried by Li and H



$$\%PIC = \frac{\delta}{e} \text{ x}100 \implies \delta = \frac{\%PIC \text{ x } e}{100} = \frac{77 \text{ x } 1.6.\,10^{-19}}{100} = 1.23\ 10^{-19}C$$

2. The length of the Li-H bond

$$\mu_{Li-H} = \delta\, d_{Li-H} \implies d_{Li-H} = \frac{\mu_{Li-H}}{\delta} = \frac{5.88 \text{ x } 3.33\ 10^{-30}}{1.23\ 10^{-19}} = 1.59\ 10^{-10}\text{ m} = 1.59\ \text{Å}$$

Exercise 10:

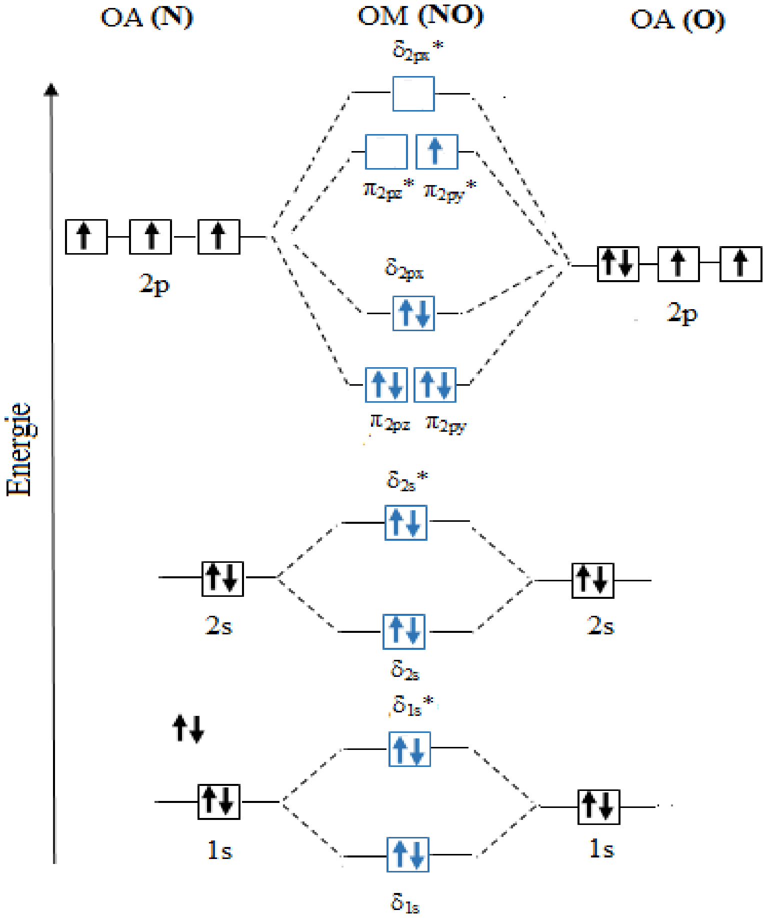
1- The Energy Diagram and Electronic Structure

$_7$N: $1s^2/2s^22p^3$

$_8$O: $1s^2/2s^22p^4$

Oxygen is more electronegative than nitrogen, so the energy levels of oxygen are lower than those of nitrogen (electrons are more stable on oxygen).

$Z_{NO} = 15 < 14$, therefore, the molecular orbital (δ_{2px}) is more energetic than the molecular orbitals (π_{2py}) and (π_{2pz}).



The electronic structure of the NO molecule: $(\delta_{1s})^2 < (\delta_{1s}^*)^2 < (\delta_{2s})^2 < (\delta_{2s}^*)^2 < (\pi_{2py})^2 = (\pi_{2pz})^2 < (\delta_{2px})^2 < (\pi_{2Py}^*)^1$.

2. The highest energy-occupied molecular orbital is the π_{2Py}^* orbital.

3. The NO molecule is paramagnetic because it has a single unpaired electron.

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