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COURSE HANDOUTS :

STRUCTURE OF MATTER (CHEMISTRY I)

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Preface

This course document, titled **"Structure of Matter (Chemistry I),"** is a comprehensive 110-page pedagogical manual designed specifically for first-year students in **Technology Sciences (TS)** and preparatory science programs. Developed at the Faculty of Applied Science at **Ibn-Khaldoun University of Tiaret**, the manual aligns with the official Ministry curriculum. It serves as an essential learning tool, synthesizing extensive teaching experience into a structured format that includes clear definitions, fundamental laws, and numerous educational diagrams and solved exercises to reinforce theoretical concepts.

The introductory chapters establish the physical and historical foundations of chemistry. The **first chapter** provides a brief but essential review of the states of matter, atoms, molecules, and solutions. This is followed by a **second chapter** dedicated to the constituents of the atom, focusing on the discovery of the electron, proton, and neutron. It highlights the landmark experiments of scientists such as **Crookes, Thomson, Millikan, and Goldstein**, while also detailing the physical properties of atoms, the nature of isotopes, and their separation through Bainbridge and Dempster spectroscopy. The **third chapter** examines spontaneous and induced nuclear reactions, focusing on the kinetics and activity of radioactive decay.

The core of the document lies in the **fourth chapter**, which transitions from classical atomic models to modern quantum mechanics. It explores the quantization of energy, wave-particle duality, and the optical spectrum of hydrogen before introducing the

Schrödinger wave equation and Heisenberg's uncertainty principle. This section meticulously outlines the rules for electronic configuration, including **Pauli's Exclusion Principle, Klechkowski's Rule, and Hund's Rule**, while also explaining the differences between core and valence electrons and the magnetic properties (paramagnetism and diamagnetism) of atomic systems.

The final portion (**chapter five**) focuses on the **periodic classification of elements** and the structural logic of the modern **periodic table**. It provides an in-depth analysis of periodic trends, such as **atomic** and **ionic radii**, **ionization energy**, and **electron affinity**. Furthermore, it compares various electronegativity scales, including those of **Pauling, Mulliken, and Allred-Rochow**. While the author has ensured the document is a rigorous and logical synthesis of material science, it remains open to constructive feedback from the academic community to address any potential inaccuracies.

Dr. HALFADJI Ahmed

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Chapter I

Fundamental Concepts

I.1 States of Matter and Macroscopic Properties

In physics, a state of matter refers to one of the three classical phases that any substance can assume in nature. Traditionally, matter exists in three primary states: solid, liquid, and gas. The state in which a given substance exists depends not only on its intrinsic properties but also on external factors such as temperature and pressure.

For instance, water can exist in three distinct states: solid (ice, snow), liquid (water), and gaseous (water vapor), depending on the surrounding temperature and pressure. In other words, matter is defined as anything that has mass and occupies space. This includes all objects, as well as substances like air, water, and oil, which are all forms of matter.

Different forms of matter are referred to as physical states, and their classification is based on the degree of molecular cohesion within the substance. The stronger the intermolecular forces, the more rigid the structure (solid); conversely, weaker interactions lead to fluidity (liquid) or dispersion (gas).

These distinct states exhibit unique physical properties, which can be described by fundamental laws of physics. Key characteristics include:

- ✓ Malleability (the ability to deform under stress),
- ✓ Viscosity (resistance to flow),

-The Ideal Gas Law, which governs the behavior of gases under varying conditions of pressure, temperature, and volume.

I.2. Phase Transitions and Changes in the States of Matter

From a microscopic perspective, the states of matter correspond to a substance composed of atoms and possessing mass, with the atom being its fundamental constituent. From a macroscopic perspective, the states of matter include the solid state, the liquid state, the gaseous state, and plasma, the fourth state of matter.

- **Solids:** The solid state has a defined volume and shape. (The particles are very close to one another; there is a strong attractive force between the particles). Solids have a definite shape because, when no external forces are applied to them, they maintain the same shape (Figure 1).
- **Liquids:** Liquids have a defined volume but no specific shape; they take the shape of their container. (The particles are close to each other, but there is space between them; the attractive force between the particles is weaker than in solids) (Figure1).
- **Gases:** Gases have neither a defined volume nor a fixed shape; they take both the volume and shape of their container. (The particles are very far apart; the attractive force is very weak, as is the gravitational force) (Figure 1).

Figure 1. solid state of matter and liquid state of matter .

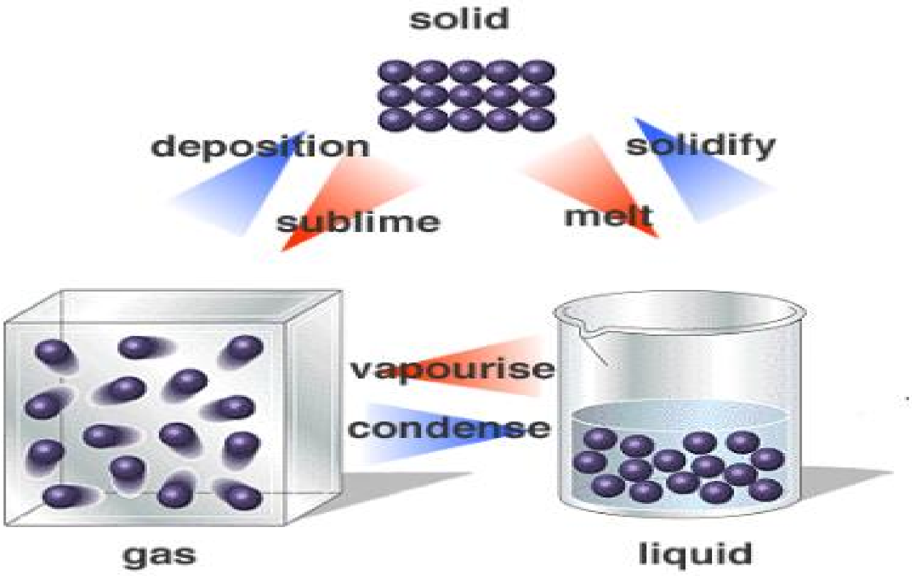


Figure 2. The solid, liquid and gas phases of matter.

I.3 Characteristic Quantities of Matter and Its States

In the natural sciences, a physical quantity (or simply a quantity) is any property that can be measured or calculated. Its values are expressed as a number, either real or complex, and are almost always accompanied by a specific unit of measurement.

There are four primary quantities used to characterize matter and its physical states:

I.4 Volume and Mass

Mass and volume are two fundamental and interrelated characteristics of any physical body.

- Mass (m): A quantity that represents the amount of matter contained within a body. It is an intrinsic property and is measured using a balance.
- Volume (V): A quantity that indicates the physical space occupied by a body. For liquids, it is commonly measured using a graduated cylinder.

In summary, mass indicates how much matter is present, while volume indicates how much space that matter takes up.

I.4.1 Volume

All objects occupy space. A body with a larger volume physically displaces more space than one with a smaller volume.

- ✓ SI Unit: The standard unit of measurement for volume is the cubic meter (m^3).
- ✓ Scale: Volume is a quantitative measure. For example, a body with a volume of 4 m^3 occupies exactly twice the space of a body with a volume of 2 m^3.

- ✓ Common Units: In laboratory and everyday settings, volume is frequently expressed in liters (L) or its submultiples (dL, cL, mL).

Unit Equivalence:

It is important to remember the relationship between cubic measure and capacity:

- 1 dm^3 = 1 L
- 1 cm^3 = 1 mL

I.4.2 Mass

All physical objects are composed of matter. Mass is the physical quantity that quantifies the amount of matter contained within a body.

- ✓ SI Unit: The standard unit for mass is the kilogram (kg).
- ✓ Common Units: The gram (g) and its multiples/submultiples are frequently used in laboratory settings:
    - Multiples: Hectogram (hg), Decagram (dag).
    - Submultiples: Decigram (dg), Centigram (cg), Milligram (mg).
- Proportionality: Mass is an additive property. For example, a body with a mass of 4 kg contains exactly twice the amount of matter as a body with a mass of 2 kg.

I.4.3 Concept of Density

Because mass and volume vary proportionally for a given substance under constant conditions, we can define density (ρ). Density represents the mass per unit volume of a substance and is typically expressed in kilograms per liter (kg/L) or grams per cubic centimeter (g/cm^3).

Property: The mass and volume of a homogeneous substance are proportional quantities.

I.5 Pressure and Temperature

Pressure and temperature are state variables that are often intrinsically linked, particularly in gases. A variation in one frequently results in a variation in the other.

Gay-Lussac's Law: This law states that for a fixed mass of gas at a constant volume, the pressure (P) is directly proportional to its absolute temperature (T):

$$\frac{P}{T} = Constant$$

I.5.1 Pressure

Pressure (P) is defined as the magnitude of the perpendicular force (F) exerted per unit area (S) of a surface.

$$P = \frac{F}{S}$$

- ✓ SI Unit: The Pascal (Pa), where 1 Pa = 1 N/m^2.
- ✓ Practical Units: Because the Pascal is a very small unit, several others are commonly used in science and industry:
    - ▪ Bar: 1 bar = 10^5 Pa.
    - ▪ Atmosphere (atm): 1 atm = 101,325 Pa (standard pressure at sea level).
    - ▪ Millimeter of Mercury (mmHg): 1 mmHg = 133.3 Pa (also known as a Torr).

I.5.2 Temperature

Temperature (*T*) is a physical quantity that provides an objective measurement of the "hotness" or "coldness" of a body. Microscopically, temperature is a measure of molecular agitation: as temperature increases, the kinetic energy of the molecules increases, leading to higher velocity and greater molecular disorder.

- SI Unit: Kelvin (K). Note that the Kelvin scale is absolute; 0 K represents the total absence of molecular motion.
- Common Scales: Degree Celsius (°C) and Degree Fahrenheit (°F).
- Ambient Temperature: Refers to the temperature of the immediate surrounding environment.

I.6 Phase Changes of Matter

A phase change (or state change) occurs when matter transitions from one physical state (solid, liquid, or gas) to another (Figure 3). These transitions are typically driven by changes in **temperature**, **pressure**, or both. Each substance undergoes these transformations at specific, characteristic temperatures (such as the melting point or boiling point).

Table 1. Transitions from physical states of matter

Initial State	Final State	Process Name
Solid	Liquid	**Fusion (Melting)**
Liquid	Gas	**Vaporization**
Solid	Gas	**Sublimation**
Gas	Solid	**Deposition (Desublimation)**
Gas	Liquid	**Liquefaction (Condensation)**
Liquid	Solid	**Solidification (Freezing)**

I.6.1 Characteristics of Phase Changes

During a phase change, **mass is conserved**, but **volume typically changes**. Microscopically, the molecules themselves remain intact; only their spatial arrangement and the forces of attraction between them are altered.

a) Physical Change

A physical change is a transformation that does not alter the chemical nature or molecular identity of a substance. It involves a change in state, shape, or physical dimensions (e.g., the melting of ice into liquid water).

b) Chemical Change

A chemical change is a transformation that alters the nature of a substance through a chemical reaction, resulting in the formation of new substances with different properties.

- ✓ Corrosion: Iron (Fe) reacts with oxygen to form rust (iron oxide).
- ✓ Combustion: Wood reacts with oxygen to form ash, carbon dioxide, and water vapor.

I.6.1.1 Fusion (Melting)

Fusion is the transition from a solid state to a liquid state. For a pure substance, fusion occurs at a specific, constant temperature known as the **melting point**. During the transition, the temperature remains constant even as heat is added, as the energy is used to break the bonds of the solid lattice.

I.6.1.2 Solidification (Freezing)

Solidification is the transition from a liquid state to a solid state. While liquid water is cooled, once it begins to freeze, the temperature of the water-ice mixture remains constant at **0°C** until all the liquid has solidified. Only after total solidification will the temperature of the ice continue to drop to the ambient temperature of the environment (e.g., –18°C in a freezer).

I.6.1.3 Sublimation and Deposition

Sublimation is the direct transition from a solid state to a gaseous state without passing through the liquid phase.

- Examples: Naphthalene (mothballs) and camphor sublime at room temperature. In very cold, dry weather, ice can sublime directly into water vapor.
- Deposition: The reverse process (gas to solid) is often called deposition or desublimation (e.g., frost forming on a window).

I.6.1.4 Liquefaction (Condensation)

Liquefaction is the transition from a gaseous state to a liquid state.

- Critical Temperature: Every gas has a characteristic **critical temperature** (T_c). Above this temperature, the gas cannot be liquefied, regardless of the pressure applied.

- Example: Nitrogen has a T_c of **–147°C**. It must be cooled below this point to be stored as a liquid. Liquid nitrogen is commonly used in dermatology for cryotherapy.

I.6.1.5 Vaporization

Vaporization is the transition from a liquid state to a gaseous state. It occurs in two ways:

- ✓ Evaporation: A surface phenomenon occurring at temperatures below the boiling point.
- ✓ Boiling: A bulk phenomenon occurring at a specific temperature where the vapor pressure equals the external atmospheric pressure.
- ✓ Pressure Dependency: The boiling point decreases as atmospheric pressure decreases.
    - Sea level: 100°C.
    - Mont Blanc: ~85°C.
    - Mount Everest: ~72°C.

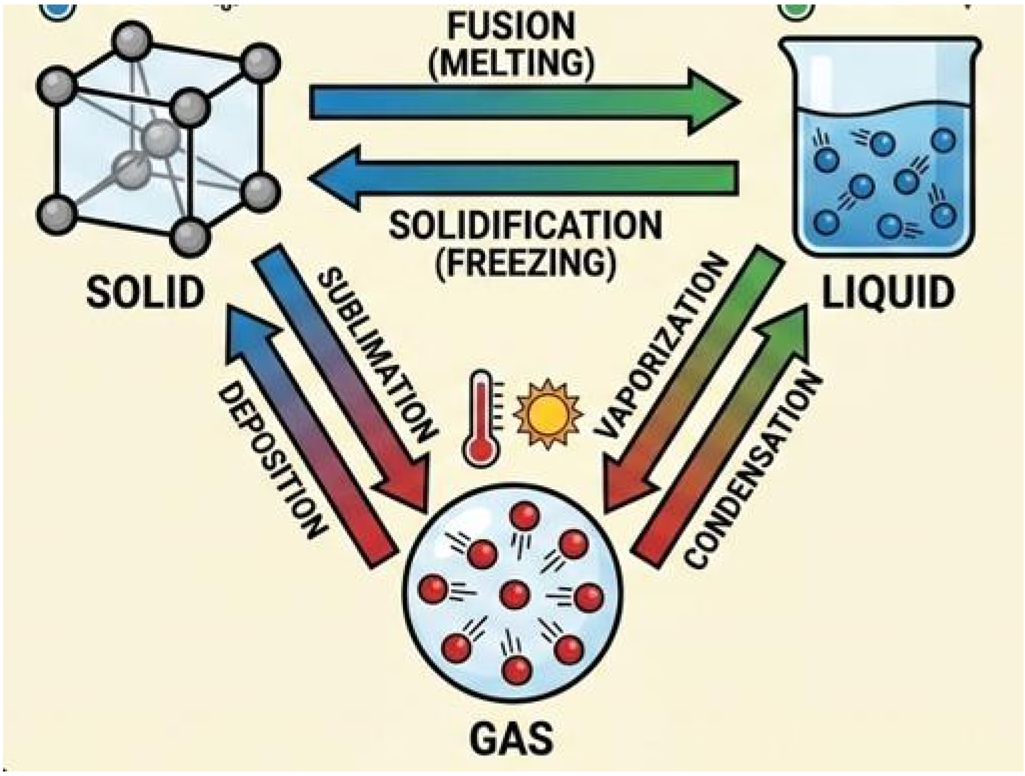


Figure 3: Process on phase changes of matter.

I.7 The Concept of the Atom

The concept of the atom was first introduced by the Greek philosopher **Democritus**, who envisioned it as the smallest, indivisible constituent of matter. However, it remained a philosophical idea until the 19th century, when scientists like **John Dalton** and **Amedeo Avogadro** established the foundations of modern atomic theory. It was only in the early 20th century that the technical means were developed to probe the subatomic structure of matter.

I.7.1 Structure of the Atom

- An atom is primarily composed of two regions:
- The Nucleus: Located at the center of the atom, it contains nucleons, which include:
    - ✓ Protons: Positively charged particles.
    - ✓ Neutrons: Electrically neutral particles. As a result, the nucleus always carries an overall positive charge.
  - The Electron Cloud: Negatively charged electrons orbit the nucleus in specific regions of space.

I.7.2 Characteristics of Subatomic Particles

The identity and behavior of an atom are determined by its constituent particles. The charges of the proton and electron are equal in magnitude but opposite in sign.

Table 2. Mass and Electrical Charge of Elementary Atomic Constituents

Particle	Electrical Charge (C)	Mass (kg)
Proton	$+1.602\ 10^{-19}$	$1.673\ 10^{-27}$
Neutron	0	$1.675\ 10^{-27}$
Electron	$-1.602\ 10^{-19}$	$9.109\ 10^{-31}$

Note: While you do not need to memorize these exact values, it is important to recognize the scale of these masses (magnitude of 10^{-27} kg). Notice that the electron is nearly **2,000 times lighter** than a proton or neutron, meaning the mass of an atom is concentrated almost entirely in the nucleus.

I.7.3 Molecules

Atoms combine to form **molecules**, which are the smallest units of a chemical compound that retain its chemical properties. A molecule consists of at least two atoms, either of the same element or different elements, held together by strong **chemical bonds**.

- ✓ Stability: These atoms do not separate spontaneously; a chemical reaction is required to alter or break the bonds within a molecule.
- ✓ Chemical Formula: A molecule is represented by a symbolic formula. This formula indicates the types of atoms involved and their quantity (indicated by subscripts).

Example: The Water Molecule

- Composition: Contains 2 atoms of Hydrogen and 1 atom of Oxygen.
- Chemical Formula: H_2O.

I.7.4 The Mole

The **mole** is the SI unit for the amount of substance. It represents a collection of N (6.023 x 10^{23}) identical entities (atoms, molecules, or ions). This unit is essential for transitioning from the microscopic scale of atoms to the macroscopic scale of the laboratory.

- ✓ Symbol: mol
- ✓ Variable: n
- ✓ Definition: A mole is defined as the number of atoms contained in exactly 12 grams of carbon-12 (^{12}C).
- ✓ Value: 1 mol = 6.023 x 10^{23} entities.

The number of moles in a sample is the ratio of its mass to its molar mass:

$$n = \frac{m}{M}$$

Where:

- *n*: Amount of substance (mol)
- *m*: Mass of the sample (g)
- *M*: Molar mass of the substance (g/mol)

I.7.5 Avogadro's Number (NA)

Avogadro's number (N_A) is the proportionality factor that relates the number of constituent particles in a sample with the amount of substance in that sample.

$$N_A = 6.023\ 10^{23}\ \text{entities/mol}$$

I.8 Units and Molar Quantities

I.8.1 Atomic Mass Unit (amu or u)

Because the masses of subatomic particles are extremely small, we use the atomic mass unit (amu).

- Definition: 1/12 of the mass of one atom of carbon-12.
- Conversion: $1\ amu = 1.66\ x10^{-27}\ kg = = 1.66\ x10^{-24}\ g$.

I.8.2 Atomic and Molecular Molar Mass

- Atomic Molar Mass: The mass of one mole of atoms of a specific element (e.g., M (O) = 16.0 g/mol.
- Molecular Molar Mass: The sum of the atomic molar masses of all atoms in a molecule.
    - ✓ Example (Water, H_2O):

$M\ (H_2O\ ) = (2 \text{ x } M\ (H)) + (1 \text{ x } M\ (O)) = (2 \text{ x } 1.0) + 16.0 = 18.0\ g/mol$

I.8.3 Molar Volume (Vm)

The molar volume of a gas is the volume occupied by one mole of that gas under specific conditions of temperature and pressure.

a) STP (Standard Temperature and Pressure):

STP is defined by a standard temperature of **0°C** (273.15 K) and a standard pressure of **1 atm** (101,325 Pa or 1.013 x 10^5 Pa).

- Note on Modern Standards: While **1 atm** is commonly used in many textbooks, IUPAC (International Union of Pure and Applied Chemistry) currently defines the standard pressure for STP as **1 bar** (10^5 x Pa or 0.987 atm).
- Molar Volume: At STP (1 atm and 0 °C), one mole of an ideal gas occupies a volume of **22.414 L**.

b) NTP (Normal Temperature and Pressure):

NTP is typically used to represent common laboratory conditions. Unlike STP, the standard temperature for NTP can vary depending on the governing body:

- Temperature **(*T*):** Usually set at **20°C** (293.15 K) or **25°C** (298.15 K).
- Pressure **(*P*):** Fixed at **1 atm** (101,325 Pa) or **1 bar** (10^5 Pa).

I.8.4 Molar Volume (V_m) at 25°C:

Under these conditions (25°C and 1 bar), the molar volume of an ideal gas is:

$$V_m = 24.79\ L/mol$$

The molar volume is the ratio of the volume (V) occupied by a substance to its amount of substance (n):

$$V_m = \frac{V}{n}$$

I.9 Gravimetric Laws

I.9.1 Law of Conservation of Mass (Lavoisier)

In a chemical reaction, matter is neither created nor destroyed. The total mass of the reactants equals the total mass of the products.

$$\Sigma m\ (reactants) = \Sigma m\ (products)$$

I.9.2 Law of Definite Proportions (Proust)

A chemical compound always contains exactly the same proportion of elements by mass, regardless of its source or method of preparation.

I.9.3 Law of Multiple Proportions (Dalton)

If two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small whole numbers.

I.9.4 Qualitative Classification of Matter

Matter can be classified based on its composition and uniformity:

Table 3. Classification of Matter: Substances and Mixtures

Type	Description	Example
Pure Substance	Composed of only one type of entity.	Distilled water, Copper.
Simple Substance	Pure substance made of only one element.	O_2, Fe, N_2.
Compound	Pure substance made of different elements.	NaCl, H_2O.
Homogeneous Mixture	Uniform appearance; components not visible.	Saltwater, Air.
Heterogeneous Mixture	Non-uniform; components are visible.	Oil and Water, Sand.

I.10 Quantitative Aspect of Matter (Concentrations)

I.10.1 Molar Concentration (Molarity)

Molarity (M or C_M) is defined as the number of moles of solute dissolved in one liter of total solution. It is the most commonly used unit of concentration in chemical laboratories.

$$C_M = \frac{n_{solute}}{V_{solution}}$$

- Units of molarity: mol/L or M.

- Note: Molarity is temperature-dependent because the volume of a liquid expands or contracts with temperature changes.

I.10.2 Molality

Molality (*m* or *Cₘ*) is defined as the number of moles of solute per kilogram of **solvent** (not solution).

$$C_m = \frac{n_{solute}}{V_{solvent\,(kg)}}$$

I.10.3 Normality (N)

Normality (N) is a measure of concentration that expresses the number of **gram equivalents** of a solute per liter of solution. It is particularly useful in titration calculations involving acid-base or oxidation-reduction (redox) reactions.

- **Unit:** equivalents per liter (eq/L) or Normal (N).

- **The Gram Equivalent:** This is the amount of substance that provides or reacts with one mole of a specific reactive species (such as H^+, OH^-, or electrons e^-).

The Normality of a solution is calculated as:

$$N = \frac{Number\ of\ gram\ eqivalents}{V_{solution\,(L)}}$$

Normality is directly related to Molarity (C_M) by a factor z, which represents the number of active species (equivalents) per molecule of solute:

$$N = z \times C_M$$

I.10.4 Mass Fraction (wi)

The ratio of the mass of a component to the total mass:

$$w_i = \frac{m_i}{m_{total}}$$

I.10.5 Mole Fraction (Xi)

The ratio of the moles of a component to the total moles:

$$X_i = \frac{n_i}{n_{total}}$$

I.10.6 Specific Gravity (d)

The ratio of the density of a substance to the density of water (1.0 g/cm^3):

$$d = \frac{\rho_{substance}}{\rho_{water}}$$

I.10.7 Dilution

During dilution, the amount of solute remains constant ($n_{initial} = n_{final}$):

$$C\_i \, V\_i = C\_f \, V\_f$$

I.10.8 Density (ρ)

Density is an intensive physical property defined as the mass of a substance per unit of volume at a specific temperature and pressure. It reflects how tightly matter is packed within a given space.

The density (ρ) is calculated using the formula:

$$\rho = \frac{m}{V}$$

Where:

- ρ : Density
- m : Mass of the substance (measured in grams or kilograms)
- V : Volume occupied by the substance (measured in milliliters, liters, or cubic meters)

While the density of a substance is constant for a given state of matter, its numerical value depends on the units used:

- SI Unit: The standard unit is the kilogram per cubic meter (**kg/m^3**).
- Common Laboratory Units:
  - ✓ For solids and liquids: grams per cubic centimeter (**g/cm^3**) or grams per milliliter (**g/mL**).
  - ✓ For gases: grams per liter (**g/L**).

Density is typically expressed in g/cm^3 for solids or g/mL for liquids. However, in SI units, it is expressed in kg/m^3:

- Standard Equivalency: 1 g/cm^3 is equal to 1000 kg/m^3.
- Unit Consistency**:** The units g/mL and g/cm^3 are identical (1 g/mL = 1 g/cm^3).

I.11 Density and Specific Gravity of a Liquid

In many scientific contexts, the term "density" (d) of a liquid often refers to its **Specific Gravity** (relative density). This is a dimensionless quantity (it has no units) that expresses the ratio of the mass of a volume of substance to the mass of an equal volume of reference material—typically water.

$$d = \frac{\rho_{substance}}{\rho_{water}}$$

Where:

- $\rho_{substance}$: Density of the substance.
- ρ_{water}: Density of pure water at 4°C (approximately 1 g/cm^3 or 1000 kg/m^3).

I.11.1 Laws of Dilute Solutions: Raoult's Law

Raoult’s Law describes the vapor pressure of a component in an ideal solution. It states that at a constant temperature, the partial vapor pressure of each component in an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the liquid phase.

For a component i in a solution:

$$P_i = X_i \,.\, P^0_i$$

Where:

- P_i: The partial vapor pressure exerted by component i above the solution.
- X_i: The mole fraction of component i in the liquid solution.
- P^0_i: The vapor pressure of the pure component i at the same temperature.

I.12 Ebulliometry (Boiling Point Elevation)

Adding a non-volatile solute to a solvent lowers its vapor pressure, causing the boiling point to increase. This elevation ($\Delta \boldsymbol{T_b}$) is proportional to the solution's molality.

The Equation: $$\Delta \boldsymbol{T_b} = \boldsymbol{T_{solution}} - \boldsymbol{T_{solvent}} = \boldsymbol{i}.\boldsymbol{K_b}\,.\boldsymbol{m}$$

Where : ***i:*** Van 't Hoff factor. $\boldsymbol{K_b}$: Ebullioscopic constant. ***m:*** Molality (moles of solute per kg of solvent).

I.13 Cryoscopy (Freezing Point Depression)

The presence of solute particles prevents the solvent from forming a solid crystal lattice at its normal temperature, resulting in a lower freezing point (ΔT_f).

The Equation: $$\Delta \boldsymbol{T_f} = \boldsymbol{T_{solution}} - \boldsymbol{T_{solvent}} = -\,\boldsymbol{i}.\boldsymbol{K_f}\,.\boldsymbol{m}$$

- Where : ***i:*** Van 't Hoff factor. $\boldsymbol{K_f}$: Croscopic constant. ***m:*** Molality (moles of solute per kg of solvent).

Chapter II

Principal Constituents of Matter

Introduction

The concept of the atom dates back more than 2,500 years to Ancient Greece, where philosophers such as Democritus proposed that all matter is composed of tiny, indivisible particles called ***atomos*****.** However, for centuries, this remained a philosophical idea rather than a scientific one.

It was not until the early 19th century, through the work of **John Dalton** and **Amedeo Avogadro**, that the atom transitioned from a philosophical abstraction to a concrete scientific concept. By the early 20th century, new technical means allowed scientists to probe matter at the subatomic scale, revealing the complex internal structure of what was once thought to be indivisible.

II.1 Dalton’s Atomic Theory

John Dalton, a British chemist, formalized the modern atomic theory by establishing several key postulates:

1. Composition of Matter: Ordinary matter is made up of extremely small "particles" called atoms.
2. Scale: These atoms are far too small to be seen with the naked eye.
3. Atomic Mass: Different chemical substances are composed of specific types of atoms, each characterized by a unique atomic mass.

4. Uniformity: All atoms of the same chemical element are identical in their physical and chemical properties.
5. Chemical Combination: Atoms combine in simple, whole-number proportions to form new substances (compounds).
6. Conservation: During chemical reactions, atoms remain unchanged in their essence; they are rearranged, but they cannot be divided, created, or destroyed.

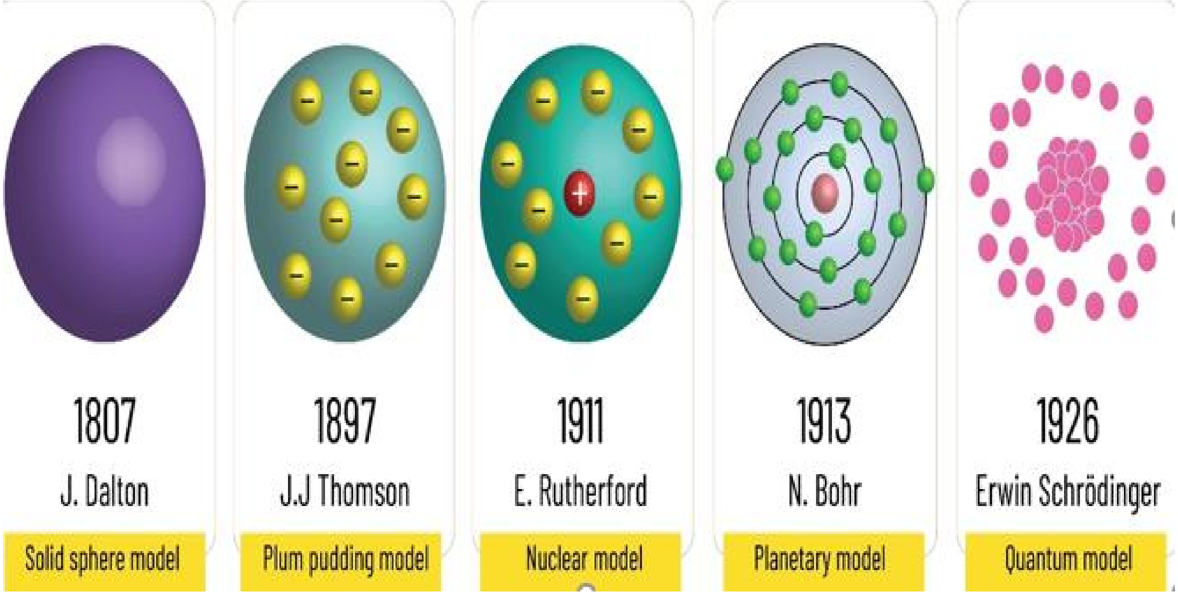


Figure 4 : Atomic models

With the exception of a few necessary updates, Dalton's first five points remain fundamental to our understanding of chemistry. However, scientific advancements in the 20th century led to two major corrections:

- Isotopes: We now know that atoms of the same element can have different masses (isotopes), requiring a slight modification to the idea that all atoms of an element are identical.

- Subatomic Particles: It was demonstrated that the final point regarding indivisibility was incorrect. Atoms can indeed be divided into more fundamental subatomic particles: **protons**, **neutrons**, and **electrons**.

II.2 Faraday's Experiment: Relationship Between Matter and Electricity

Michael Faraday observed with "astonishment" that the breaking of chemical bonds through electrolysis involved significant and quantifiable amounts of electricity. This established the first direct link between chemical affinity and electrical charge.

II.3 The Laws of Electrolysis and the Atomic Nature of Charge

In 1833, Michael Faraday established the **Laws of Electrolysis**, which demonstrated that in an aqueous salt solution, each atom or molecular fragment carries a fixed, discrete electric charge. These laws were a major contribution to atomic theory throughout the 19th century.

The Concept of Quantized Charge: Faraday established that for a constant quantity of electricity, the mass of the substance decomposed at the electrodes is directly proportional to its **equivalent weight**. This observation laid the groundwork for the concept of the electron as a fundamental particle carrying a unit of electric charge, although the particle itself was not isolated until decades later.

II.3 Identification of the Constituents of Matter and Their Physical Properties

To understand the structure of the atom, scientists had to determine the physical properties (mass and charge) of its fundamental components.

II.3.1 The Electron

II.3.1.1 Discovery and Characterization

The term **"electron"** was first introduced by **G. Johnstone Stoney** in 1891 to describe the "fundamental unit quantity of electricity." However, the experimental demonstration and characterization of the electron as a physical particle were achieved by **J.J. Thomson** in 1897.

Through his experiments with cathode rays, Thomson proved that matter is not indivisible. He demonstrated that atoms consist of:

- Heavy, positively charged components (which make up the bulk of the mass).
- Light, negatively charged particles called electrons, which are universal constituents of all atoms.

Thomson's work shifted the scientific paradigm from the "indivisible atom" to a structured entity containing subatomic particles with specific mass and charge.

Table 4. Key Contributions to the Identification of Subatomic Particles

Scientist	Contribution	Key Concept
Faraday	Laws of Electrolysis	Linked electricity to chemical bonds; suggested charge is discrete.
Stoney	Nomenclature	Coined the term "electron" for the unit of charge.
Thomson	Cathode Ray Experiments	Proved the electron is a particle with mass and negative charge.

. II.3.1.2 J.J. Thomson's Experiment: Determination of the e/m_e Ratio

In 1897, J.J. Thomson conducted a series of experiments using a vacuum tube (Crookes tube) to investigate the nature of "cathode rays." His work provided the first definitive evidence that atoms are composed of smaller, subatomic particles.

Experimental Observations : When a high electrical potential (approximately 40,000 V) is applied between two electrodes in a low-pressure gas tube, a beam is emitted from the cathode. These **cathode rays** travel in straight lines perpendicular to the cathode surface toward the anode.

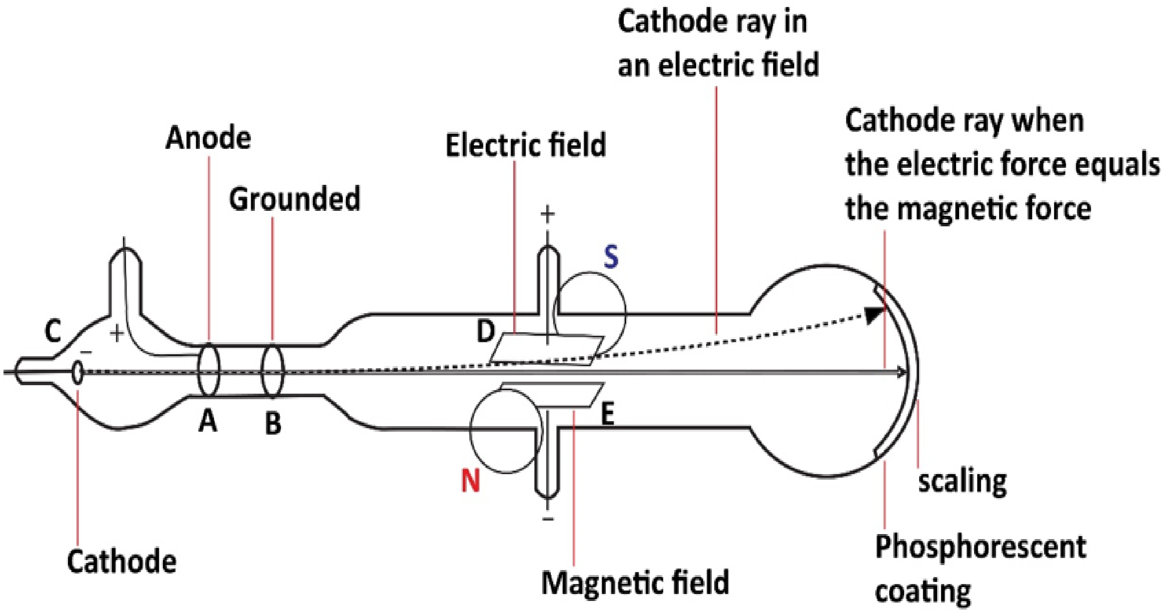


Figure 5 . J.J. Thomson cathode ray tube experiment.

The Figure 5 show the cathode ray tube, the slit to focus the beam, the charged plates for the electric field, and the coils for the magnetic field.

To determine the properties of these rays, Thomson applied external fields:

- Electric and Magnetic Fields: When subjected to these fields, the trajectory of the rays was deflected.
- Direction of Deflection: The beam was consistently deflected toward the positive plate of an electric field and in a direction dictated by the Lorentz force in a magnetic field. This confirmed that cathode rays consist of **negatively charged particles**, which were later named **electrons**.

Key Findings

1. Nature of Electrons: Cathode rays are not light or ether waves, but streams of discrete, negatively charged particles.
2. Universal Particle: Thomson found that the properties of these particles remained the same regardless of the cathode material or the gas used in the tube, suggesting electrons are a fundamental constituent of all matter.
3. Charge-to-Mass Ratio (e/m_e): By balancing the effects of the magnetic and electric fields, Thomson was able to calculate the specific charge (the ratio of the electron's charge to its mass):

$$\frac{e}{m_e} = 1.758\ 10^{11}\ C/kg$$

This experiment was revolutionary because it proved that the atom was not the smallest unit of matter. By calculating the e/m_e ratio, Thomson showed that the electron was significantly lighter than the hydrogen atom, which was the smallest known mass at the time.

II.3.1.3 J.J. Thomson's Plum Pudding Model

J.J. Thomson’s discovery of the electron in 1897 led him to propose that atoms are **divisible**, directly challenging the classical Daltonian view of the atom as an indivisible, solid sphere. To reconcile the existence of negatively charged electrons with the fact that atoms are overall electrically neutral, he introduced the **Plum Pudding Model** in 1904.

Characteristics of the Model:

- The Positive Medium: The atom is envisioned as a uniform, spherical volume of positive charge (the "pudding"). This positive charge is diffuse and spread throughout the entire volume of the atom.
- The Electrons: Negatively charged electrons (the "plums") are embedded within this positive sphere. Thomson suggested that these electrons were positioned to balance the positive charge, ensuring the atom remained electrically neutral.
- Internal Motion: In this model, the electrons were thought to be held in place by electrostatic forces but were capable of vibrating or moving within the positive matrix.

The Plum Pudding Model was the first to incorporate subatomic particles into the atomic structure. However, it was eventually disproven by **Ernest Rutherford's gold foil experiment**, which showed that the positive charge is not diffuse but is instead concentrated in a tiny, dense nucleus.

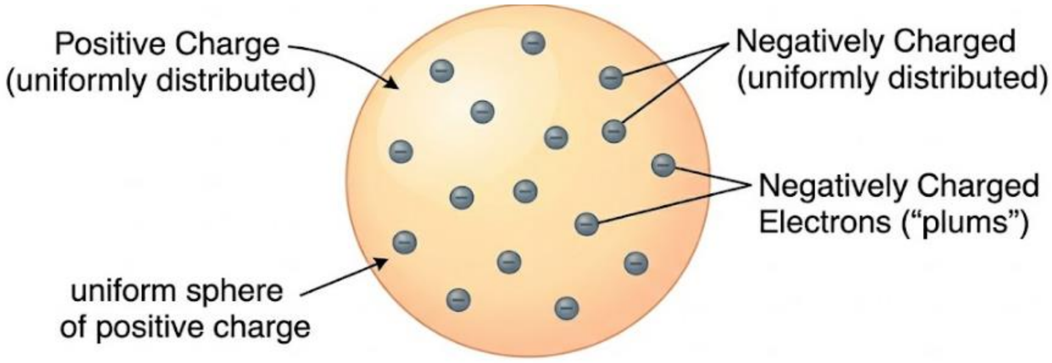


Figure 6. J.J. Thomson's "Plum Pdding " Model of the Atom

II.3.1.4 Millikan's Oil Drop Experiment: Determination of the Electron's Charge (e) and Mass (m_e)

In 1909, Robert Millikan and Harvey Fletcher performed a groundbreaking experiment to measure the elementary electric charge. By observing the motion of tiny oil droplets, they determined that electric charge is **quantized**.

Experimental Setup:

- **Atomizer (P):** A sprayer produces a fine mist of oil droplets in the upper chamber.
- **Condenser Plates:** Two horizontal metal plates create a uniform electric field. The droplets fall through a small hole in the top plate.
- **Ionization:** A beam of X-rays ionizes the air, causing free electrons to attach to the falling oil droplets, giving them a negative charge (q).
- **Microscope (M):** Used to observe the droplets and measure their terminal velocity under the influence of gravity and the electric field.

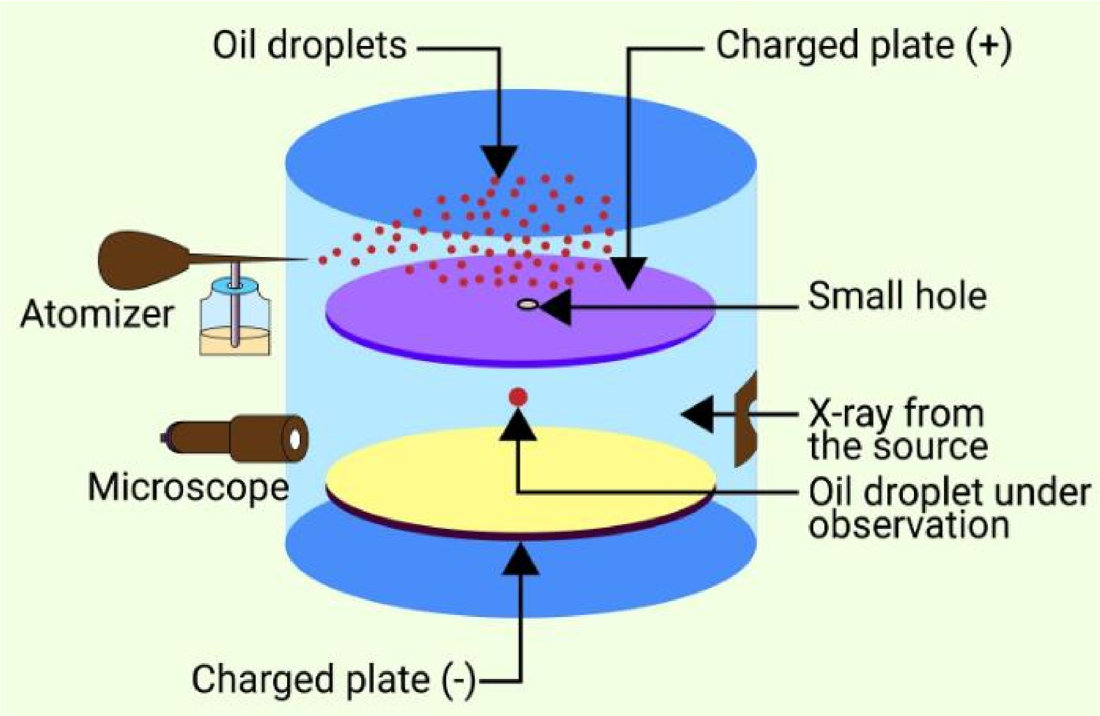
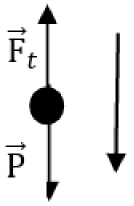


Figure 7 : Millikan's Oil Drop Experiment

By adjusting the voltage between the plates, the upward **electric force** ($F_e = q.E$) can be balanced against the downward **gravitational force** ($F_g = m.g$). By analyzing the droplets' rise and fall speeds, Millikan could calculate the total charge (q) on each drop.

a) Vertical Droplet Fall : When falling freely at a constant speed, the droplet's weight (P) is balanced by the air friction force (F_t), neglecting Archimedes' thrust.

$\overrightarrow{P} + \overrightarrow{F_t} = 0$



By projection:

$$P - F_t = 0 \quad ➔ \quad m.g = 6.\pi.\eta.r.v$$

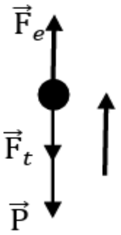
Given the density ρ and spheric volume V => $V = \frac{4}{3}\pi r^3$, we have:

$$\rho = \frac{m}{V} \;=>\; m = \rho\,.V = \rho\,.\frac{4}{3}\,\pi.r^3$$

Substituting (2) into (1):

$$r = \sqrt{\frac{9.\eta.v}{2.\rho.g}}$$

b) Droplet Ascent : Under an electric field E, a droplet with charge q moves upward. The force balance includes weight (P), friction (F_t), and electrical power (Fe):



$\overrightarrow{P} + \overrightarrow{F_t} + \overrightarrow{F_e} = m.\vec{a}$

By projection:

$$-P - Ft + Fe = 0 \quad ➔ \quad -\rho\,.\frac{4}{3}\,\pi.r^3.g - 6.\pi.\eta.r.v + qE = 0$$

The **charge (*q*)** is calculated as:

$$\boldsymbol{q} = \frac{\rho\,.\frac{4}{3}\,\pi.r^3.g + 6.\pi.\eta.r.v}{E}$$

Millikan observed that the measured charge q on any droplet was always an integer multiple of a fundamental constant, ***e*:** $\boldsymbol{q} = n \,.\, \boldsymbol{e}$ $(n = 1, 2, 3, \ldots)$

- Elementary Charge **(*e*): 1.602 x $\mathbf{10^{-19}}$** Coulombs
- Mass of the Electron **($\boldsymbol{m_e}$):** Using the charge-to-mass ratio (e/ m_e) previously discovered by J.J. Thomson, the mass was calculated as:

$$\boldsymbol{m_e = 9.109\ 10^{-31}\ kg}$$

II.3.2 The Proton

The proton is a subatomic particle found in the nucleus of all atoms. It is significantly more massive than the electron and carries a positive charge.

Physical Characteristics :

- **Size:** The proton is approximately 100,000 times smaller than the total diameter of a hydrogen atom. While the atom is roughly 10^{-10} m (1 Ångström), the proton is about 10^{-15} m (1 femtometer).
- **Charge:** It carries a single positive elementary charge (+1e), which is exactly equal in magnitude but opposite in sign to the electron’s charge: $+1.602\ 10^{-19}$ C.

Mass and the Atomic Mass Unit (u) : Because the masses of subatomic particles are extremely small when expressed in kilograms, we use the **atomic mass unit (u)**:

$$1\ u = 1.660\ 10^{-27}\ kg$$

- **Mass of a Proton ($\boldsymbol{m_p}$):**

$$m_p = 1.6726 \text{ x } 10^{-27}\ kg = 1.0073\ u$$

The figure 7 show the charged plates (anode and cathode), the X-ray source, and the microscope to help visualize the balance of forces.

II.3.3 Chadwick's Experiment: Discovery of the Neutron

The existence of a neutral subatomic particle was confirmed by **James Chadwick** in 1932. Prior to this, the atomic mass of elements could not be fully explained by protons alone, leading scientists to search for a third, neutral component of the nucleus.

Experimental Setup :

James Chadwick conducted a series of experiments based on earlier observations by Frédéric and Irène Joliot-Curie:

- ✓ **Bombardment:** He bombarded a target of **beryllium (^{9}Be)** with high-energy **alpha particles** (α, helium nuclei).
- ✓ **Emission:** This bombardment caused the beryllium to emit a highly penetrating radiation that was initially thought to be gamma rays.

Key Observations :

- ✓ Electrical Neutrality: Unlike protons or alpha particles, this new radiation was not deflected by electric or magnetic fields. This proved that the particles had no electric charge.
- ✓ Paraffin Wax Interaction: When this radiation struck a layer of paraffin wax (a substance rich in hydrogen), it knocked high-velocity protons out of the wax.
- ✓ Mass Determination: By measuring the energy and momentum of these ejected protons, Chadwick calculated that the neutral particles had a mass nearly identical to that of a proton (1.675×10^{-27}kg).

Chadwick concluded that the radiation consisted of a new subatomic particle, which he named the **neutron**. The nuclear reaction can be represented as:

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

- Completing the Nucleus: The discovery of the neutron completed the fundamental model of the atomic nucleus, establishing it as a collection of **nucleons** (protons and neutrons).
- Nuclear Stability: It explained how the nucleus stays together; neutrons provide the "nuclear glue" (strong nuclear force) that helps stabilize the repulsion between positively charged protons.
- Scientific Foundation: This discovery was essential for the later development of nuclear physics, specifically the understanding of **isotopes**, nuclear **fission**, and **fusion**.

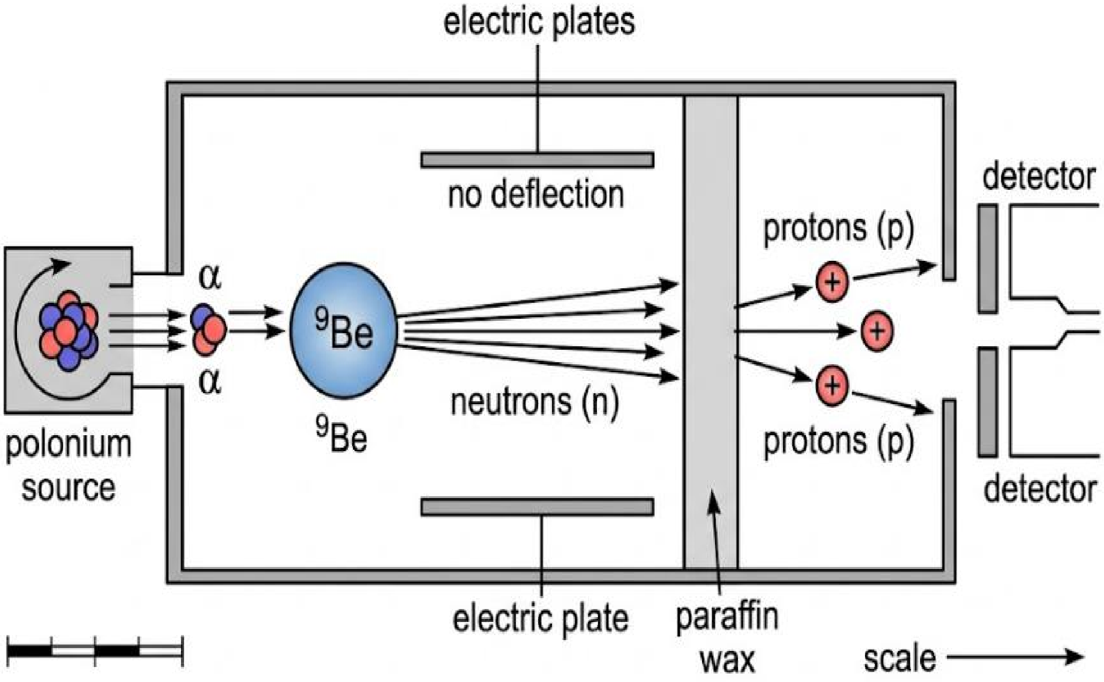


Figure 8. illustrating James Chadwick's 1932 experiment that led to the discovery of the neutron.

II.3.4 Rutherford’s Planetary Model of the Atom

The **Rutherford atomic model**, commonly known as the **planetary model**, was proposed in 1911 by Ernest Rutherford. This model replaced the **Thomson "plum pudding" model** (1904), which had suggested that an atom was a sphere of positive charge with electrons embedded throughout it. Thomson's model was famously invalidated by the results of Rutherford's **gold foil experiment** in 1909.

II.3.4.1 Discovery of the Nucleus

The discovery of the atomic nucleus is credited to Ernest Rutherford and his collaborators, Hans Geiger and Ernest Marsden. Their landmark experiments at the University of Manchester fundamentally changed our view of matter.

The gold foil experiment setup:

- Experimental Source: Alpha particles (positively charged helium nuclei) were fired at an extremely thin sheet of gold foil.
- Detection: A fluorescent screen was placed around the foil to detect the scattering angles of the particles after impact.

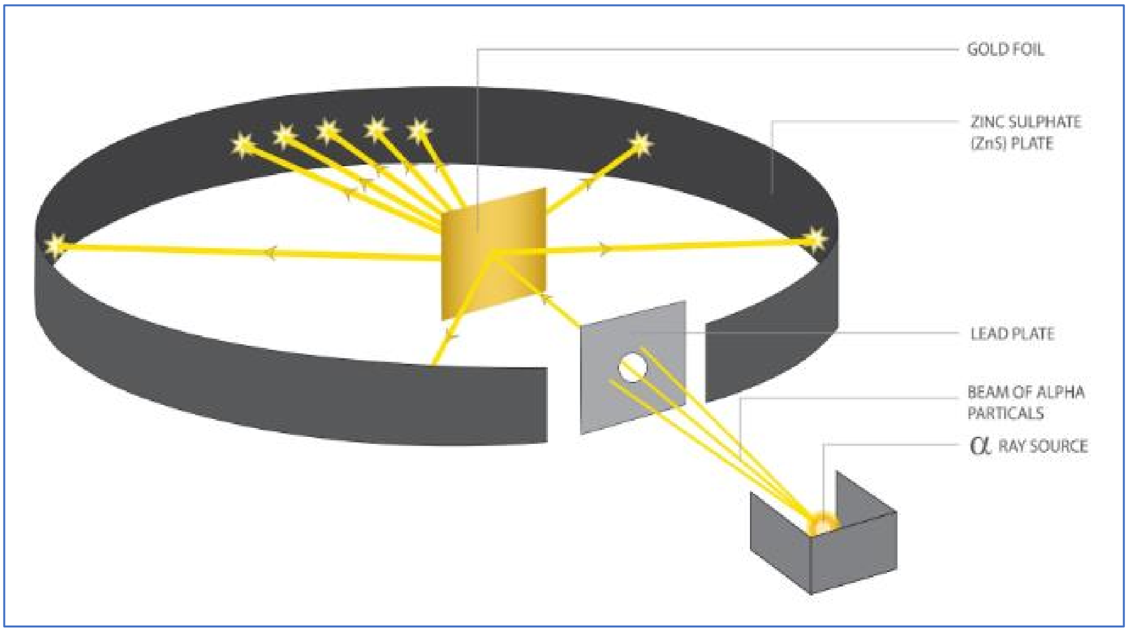


Figure 9. Rutherford gold foil experiment.

Key Observations and Conclusions:

- ✓ Most alpha particles passed directly through the foil with no deflection.
  - The atom consists mostly of **empty space**.
- ✓ A small fraction of particles was deflected at large angles.
- ✓ Roughly 1 in 8,000 particles bounced back toward the source.
  - There exists a **small, dense, and positively charged region** at the center of the atom, which contains nearly all the atom's mass. Rutherford named this the **nucleus**.

II.3.4.2 Characteristics of the Model

Based on these results, Rutherford proposed the following structure:

- **The Nucleus:** A tiny, central core containing the atom's positive charge and mass.
- **Electronic Orbitals:** Electrons move around the nucleus at relatively large distances, similar to planets orbiting the sun.
- **Atomic Volume:** Because the nucleus is so small compared to the total size of the atom, the atom is primarily composed of a vacuum (empty space).

Rutherford's discovery revolutionized physics by identifying the nucleus. However, the model had limitations; it could not explain why orbiting electrons, which are accelerating charges, do not lose energy and spiral into the nucleus. This problem was addressed shortly after by **Niels Bohr**, who refined the planetary model by introducing quantized electron shells (the **Bohr Model**).

II.3.5 The Atom

An atom is the smallest unit of matter that retains the chemical properties of an element. It consists of a dense central **nucleus** containing protons and neutrons, surrounded by a **cloud of electrons**. Atoms are electrically neutral because the number of positive protons in the nucleus is exactly balanced by the number of negative electrons in the cloud.

II.3.5.1 Atomic Nomenclature

The identity of an atom is defined by its **atomic number (Z)**, which represents the number of protons in its nucleus. Every chemical element has a unique atomic number; for example, Z=1 is always Hydrogen, Z=6 is Carbon, and Z=8 is Oxygen.

To represent a specific nucleus (or nuclide), we use the following standard notation:

$$\boldsymbol{{}_{Z}^{A}X}$$

- **X**: The **chemical symbol** of the element (e.g., O for Oxygen, Cl for Chlorine).
- **Z**: The **atomic number** (or charge number), representing the number of protons.
- **A**: The **mass number**, representing the total number of nucleons (protons + neutrons).

The number of neutrons (N) can be calculated using the relationship:

$$\boldsymbol{A = Z + N \Rightarrow N = A - Z}$$

II.3.5.2 Characteristics of the Atom

The atom is characterized by its subatomic particles, which differ in mass and charge. While the electrons "orbit" the nucleus (as described in the Rutherford model), they occupy most of the atom's volume, while the nucleus contains nearly all its mass.

Tale 5. Mass and Charge for Protons, Neutrons, and Electrons

Particle	Charge (Coulombs)	Elementary Charge	Mass (kg)
Proton	$+1.602 \times 10^{-19}$ C	+1	1.673×10^{-27} kg
Neutron	0 C	0	1.675×10^{-27} kg
Electron	-1.602×10^{-19} C	-1	9.109×10^{-31} kg

- **Mass Comparison**: An electron is approximately **1836 times lighter** than a proton. Consequently, the mass of an atom is essentially concentrated in its nucleus.
- **Strong Interaction**: Protons and neutrons (nucleons) are held together in the nucleus by the **strong nuclear force**, which overcomes the electromagnetic repulsion between the positive protons.

II.3.5.3 The Nucleus

The nucleus is the extremely dense central region of the atom. Despite its small size relative to the entire atom, it determines the element's identity and its mass. The neutrality of the atom is maintained by the equality between the number of protons (Z) and the number of electrons.

II.4 Isotopy and Relative Abundance

Isotopes are atoms of the same chemical element that possess the same number of protons (Z) but a different number of neutrons (N).

- **Chemical Properties**: Because isotopes have the same number of electrons, they exhibit nearly identical chemical behavior.
- **Physical Properties**: Because they have different mass numbers (A), they differ in physical properties such as density and atomic mass.

Example: Carbon Isotopes

- **Carbon-12** ($^{12}_{6}$C) : 6 protons, 6 neutrons.
- **Carbon-13** ($^{13}_{6}$C) : 6 protons, 7 neutrons.
- **Carbon-14** ($^{14}_{6}$C) : 6 protons, 8 neutrons.

II.4.1 The Natural Abundance of Isotopes (NA)

Isotopy is the phenomenon where different isotopes exist for the same chemical element. The **relative abundance** of an isotope refers to the proportion of that specific isotope within a naturally occurring sample of the element. This abundance varies depending on the element and its source; however, for most terrestrial applications, these proportions are considered constant.

For example, carbon exists as three natural isotopes: **carbon-12**, **carbon-13**, and **carbon-14**.

- **Carbon-12** is the most prevalent, comprising approximately **98.9%** of all natural carbon.
- **Carbon-13** accounts for about **1.1%**.
- **Carbon-14** is present only in trace amounts, representing roughly one carbon atom in a trillion.

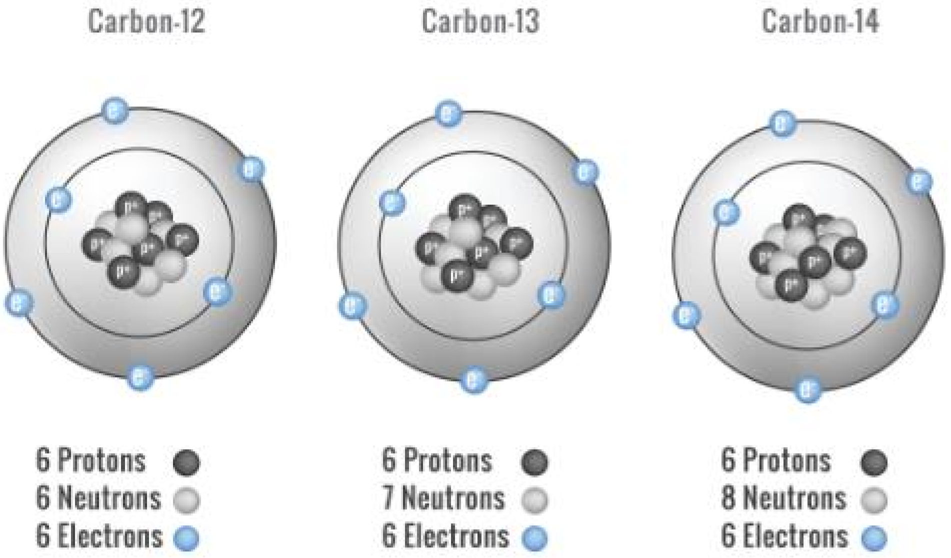


Figure 10 : Isotopes of Carbon (C12 , C13 and C14)

II.4.1.2 Average Molar Mass Calculation

The natural abundance of an isotope is equivalent to its **mole fraction** in a stable mixture. Because the proportions of these isotopes are generally constant, we can calculate the **average molar mass** (M) of an element using the following weighted average formula:

$$M = \sum(x_{i\,.}\, M_i)$$

Where:

- ***M**:* Average molar mass of the element.
- x_i: Natural abundance (mole fraction) of isotope *i*.
- M_i: Molar mass of isotope *i*.

Example: Oxygen (O)

Oxygen consists of three stable isotopes with the following distribution:

Isotope	Abundance (Molar %)	Range of Variation
^{16}O	99.757 (16)%	99.738 – 99.776
^{17}O	0.038 (1)%	0.037 – 0.040
^{18}O	0.205 (14)%	0.188 – 0.222

Calculation of the average molar mass M(O):

$$M(O) = (0.99757 \times M(^{16}O)) + (0.00038 \times M(^{17}O)) + (0.00205 \times M(^{18}O))$$

Using the approximate mass values:

$$M(O) = (0.99757 \times 16) + (0.00038 \times 17) + (0.00205 \times 18)$$

$$M(O) = \mathbf{15.999}\ g/mol$$

II.5 Isotope Separation and Determination of Atomic Mass

II.5.1 Fundamentals of Mass Spectrometry

Mass spectrometry is a powerful analytical technique used to determine the molecular mass and chemical composition of a sample. It finds applications across diverse scientific fields, including chemistry, biochemistry, pharmacology, geology, and astronomy.

The primary function of a mass spectrometer is to **separate isotopes** of the same element and measure their individual masses. This separation is achieved by exploiting the behavior of charged particles (ions) when subjected to electric and magnetic fields. The most common approach involves measuring the **mass-to-charge ratio (*m/q*)**.

Historical and Modern Instrument Types:

- **Aston Mass Spectrograph:** Historically significant for identifying isotopes.
- **Dempster Mass Spectrometer:** Known for magnetic sector focusing.
- **Bainbridge Mass Spectrometer:** Utilizes a velocity filter for high precision.

II.5.2 Components of a Mass Spectrometer

A mass spectrometer is a sophisticated instrument that analyzes a sample through a sequence of physical processes:

1) The Ion Source

The sample must first be vaporized and ionized. Several modern techniques are used depending on the nature of the sample:

- Electron Ionization (EI): Common for small molecules; uses an electron beam to knock electrons off the sample.
- Electrospray Ionization (ESI): A "soft" ionization technique ideal for large biological molecules (proteins).
- Matrix-Assisted Laser Desorption/Ionization (MALDI): Uses a laser to ionize samples embedded in a matrix.

2) The Mass Analyzer

This is the heart of the instrument where ions are separated based on their *m/q* ratio. The choice of analyzer depends on the required resolution:

- Magnetic Sector: (As seen in Bainbridge/Dempster models) uses a magnetic field to deflect ions into circular paths.
- Quadrupole: Uses oscillating electric fields to filter specific ions.
- Time-of-Flight (TOF): Measures the time it takes for an ion to travel a fixed distance.
- Ion Trap & Orbitrap: Use electromagnetic fields to "trap" and measure ions with extreme precision.

3) The Analysis Chamber (Vacuum System)

To prevent ions from colliding with air molecules, which would alter their trajectories, the entire process occurs within a high-vacuum chamber.

4) The Detector

The detector records the impact or the induced current of the separated ions. This signal is amplified and converted into a digital format.

5) The Data System (Computer)

The computer processes the detector's signal using specialized software to generate a **mass spectrum**. This spectrum is a plot of relative abundance versus the *m/q* ratio, allowing for the identification of isotopes and molecular structures.

II.5.3 Bainbridge Mass Spectrograph

The Bainbridge spectrograph is an instrument used for the precise determination of atomic masses and the relative concentrations of isotopes. It consists of four main functional parts:

- ✓ **The Ion Source:** A heated filament emits a stream of electrons that collide with gas atoms, creating positive ions.
- ✓ **The Velocity Filter (Selector):** This stage ensures all ions entering the analyzer have the same velocity.
- ✓ **The Magnetic Analyzer:** A region where ions are separated based on their mass.

- ✓ **The Ion Detector:** A photographic plate or an electrode (ion collector) that records the impact of the ions.

Principles of Operation

1) The Velocity Filter:

In this region, ions are subjected to perpendicular (orthogonal) electric *(E)* and magnetic (B_0) fields. The ions experience two opposing forces:

- **Electric Force:** $F_E = qE$
- **Magnetic Force:** $F_m = qv_0B_0$

An ion will pass through the exit slit in a straight line only if these forces are equal in magnitude ($F_E = F_m$):

$$qE = qv_0B_0 \qquad \Rightarrow \qquad v_0 = \frac{E}{B}$$

Thus, all ions exiting the filter have the same velocity v_0, regardless of their mass or charge.

2) The Analyzer:

The ions enter a second magnetic field (B) perpendicular to their motion. The magnetic force acts as a centripetal force, causing the ions to follow a circular trajectory:

$$F_{Centripetal} = \frac{mv_0^2}{R} = qv_0B$$

From this, we derive the **radius of the trajectory (R)**:

$$R = \frac{mv_0}{qB} \quad \Rightarrow \quad m = \frac{Rq}{v_0}$$

3) Isotopic Separation

Since v_0, q, and B are constant, the radius depends solely on the mass (m). For two isotopes with masses m_1 and m_2:

- $R_1 = \frac{m_1 v_0}{qB}$
- $R_2 = \frac{m_2 v_0}{qB}$

The distance **d** between the two spots on the detector corresponds to the difference in diameters:

$$\boldsymbol{d} = (R_2 - R_1) = \frac{2\,v_0}{qB}\ (m_2 - m_1)$$

By substituting $v_0 = \frac{E}{B_0}$, the **mass-to-charge ratio** is given by:

$$\frac{m}{q} = \frac{R.B.B_0}{E}$$

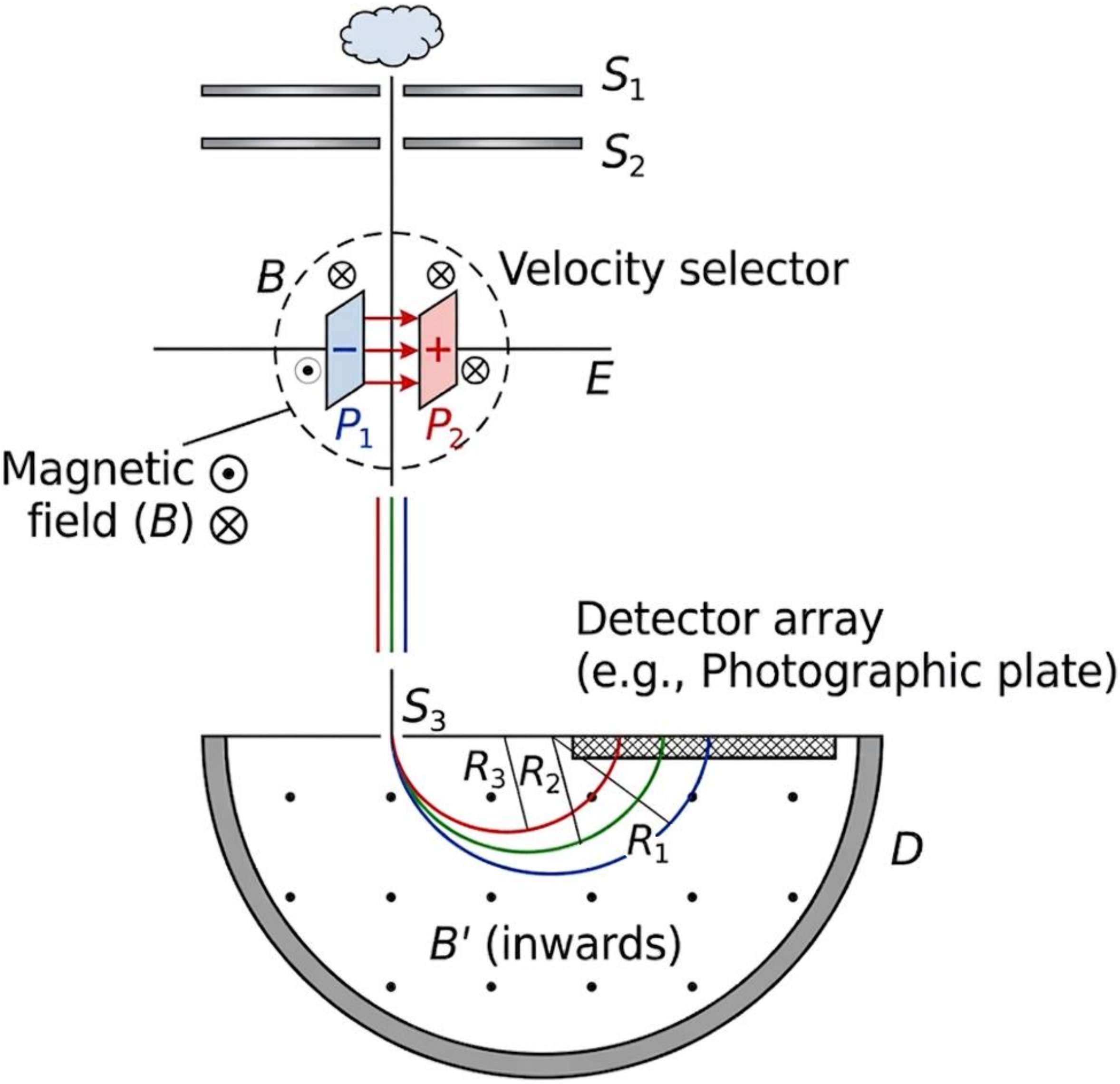


Figure 11. Bainbridge mass spectrograph

II.5.4 Dempster's Spectrograph

Invented by A.J. Dempster, this magnetic sector spectrograph was instrumental in the discovery of the Uranium-235 (^{235}U) isotope in 1935. While many models exist, they all share the common principle of using electromagnetic fields to separate ions based on their **mass-to-charge ratio (*m/q*)**.

Mechanism:

1. **Ionization and Acceleration:** Atoms or molecules are ionized by electrons emitted from a hot filament (F). They are then accelerated by an electric potential difference toward the entrance slit (S_1).
2. **Deflection:** Upon entering a uniform magnetic field, the ions experience the Lorentz force, forcing them into a semi-circular path.
3. **Detection:** The radius of the trajectory (r) is defined by the positions of the slits (S_1, S_2, S_3). Only ions with a specific $\frac{m}{q}$ ratio will successfully pass through the slits to reach the detector (D).

By varying either the accelerating voltage or the magnetic field strength, different masses can be focused onto the detector sequentially.

Chapter III:

Radioactivity and Nuclear Reactions

III.1 Natural Radioactivity

Natural radioactivity was discovered by **Becquerel in 1896**. He observed that uranyl potassium sulfate emitted invisible radiation capable of ionizing gases and developing (fogging) photographic plates.

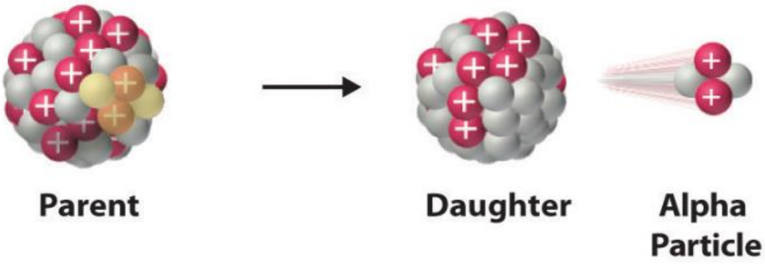
A defining characteristic of this radiation is that its rate of decay is entirely independent of external physical or chemical interventions—such as temperature, pressure, or concentration. This distinguishes **nuclear reactions** from **chemical reactions**. Radioactivity is a spontaneous process where an unstable nucleus reaches a more stable state by emitting particles or electromagnetic radiation.

III.1.1. αDecay (Alpha Radiation)

Alpha emission typically occurs in heavy nuclei with an atomic number Z >83. The nucleus ejects an alpha particle, which is a helium nucleus ${}^{4}_{2}He$, consisting of two protons and two neutrons.

General Equation:

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

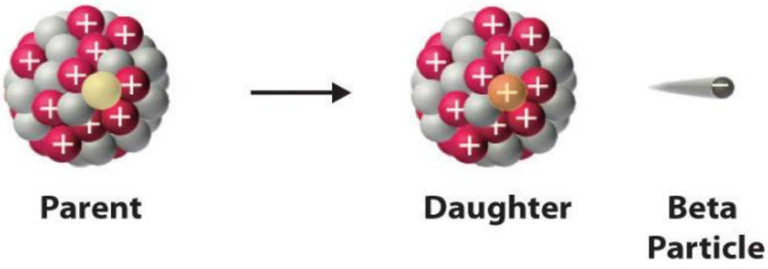


- Alpha particles are highly energetic and possess high ionizing power due to their double positive charge. However, because of their relatively large mass, they have very low penetrating power (they can be stopped by a sheet of paper or the outer layer of human skin).

III.1.2 β^- Decay (Beta-Minus Radiation)

β^- emission occurs in unstable isotopes that possess an **excess of neutrons**. To achieve stability, a neutron is transformed into a proton and an electron (called a β^- particle), which is then ejected from the nucleus.

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



Nuclear Transformation:

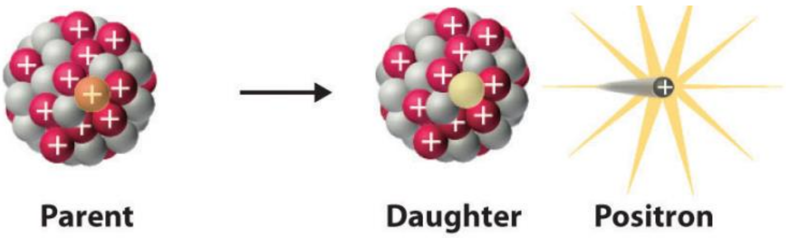
$${}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e + v_e$$

This process results in a **transmutation**, where the atomic number increases by one (Z+1), changing the identity of the element.

III.1.3. β^+ Decay (Positron Emission)

This occurs in isotopes with an **excess of protons**. The nucleus seeks stability by decreasing its atomic number. A proton is transformed into a neutron, and a **positron** ($^{0}_{1}e$) is ejected. The positron is the antiparticle of the electron; it possesses the same mass but an opposite (positive) charge.

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



Nuclear Transformation:

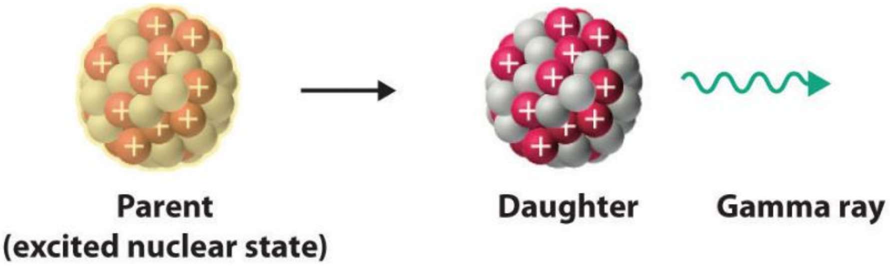
$$^{1}_{1}p \rightarrow \, ^{1}_{0}n + \, ^{0}_{1}e + \, v_e$$

Like β^- decay, this is a transmutation as the number of protons changes, effectively moving the element one position back in the periodic table.

III.1.4. γ Radiation (Gamma Rays)

Gamma radiation often accompanies α and β emissions. When a nucleus undergoes disintegration, the resulting "daughter" nucleus is frequently left in an **excited state** ($^{A}_{Z}X*$). To reach its **fundamental (ground) state**, the nucleus releases excess energy in the form of a high-energy photon known as a gamma ray.

$$^{A}_{Z}X'' \rightarrow \, ^{A}_{Z}X + \boldsymbol{\gamma}$$



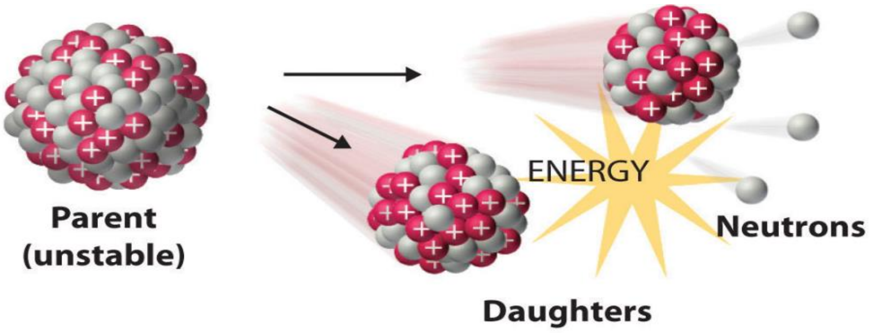
- γ rays are pure electromagnetic radiation with no rest mass or electrical charge. They possess extremely high frequency and energy, giving them significantly higher penetrating power than α or β particles, though they have a lower ionizing power.

III.2 Artificial radioactivity

III.2.1 Nuclear Fission

Nuclear fission involves the splitting of a heavy nucleus into two or more lighter nuclei of approximately equal mass. This process is triggered by the bombardment of the nucleus with a neutron. The reaction releases a significant amount of energy—approximately **200 MeV per atom**—and additional neutrons. These neutrons can subsequently strike neighboring nuclei, initiating a **nuclear chain reaction**. Example of fission Reaction:

$$^{235}_{92}U + \, ^{1}_{0}n \rightarrow \, ^{132}_{51}Sb + \, ^{101}_{41}Nb + 3^{1}_{0}n$$



III.2.2 Fusion Reaction

Nuclear fusion is the process where two or more light atomic nuclei unite to form a single heavier nucleus. This occurs under conditions of extremely high temperature and pressure (such as in the sun). During fusion, a portion of the combined mass is converted into a tremendous amount of energy.

III.2.3 Induced Transmutation Reactions

Induced transmutation occurs when a stable nucleus is transformed into a different element by bombardment with high-energy particles. The resulting nuclide typically maintains a mass number *(A)* identical or very similar to the target nucleus.

Example of neutron bombardment of Sulfur :

$$^{32}_{16}S + \, ^{1}_{0}n \rightarrow \, ^{1}_{1}p + \, ^{32}_{15}P$$

III.3 Kinetics of Radioactive Decay

III.3.1 Energy Aspect

In any nuclear reaction, although the total number of nucleons and the overall charge are conserved, there is a measurable **mass defect** (Δm). This loss of mass is converted into energy according to **Einstein's mass-energy equivalence relation**:

$$\Delta E = \Delta m \, . \, c^2$$

Where c is the speed of light (3×10^8 m/s).

III.3.2 The Law of Radioactive Decay

Radioactive decay is a first-order kinetic process. The rate of decay (the number of atoms *dN* disintegrating over a time interval *dt*) is directly proportional to the number of radioactive nuclei (*N*) present at that moment:

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

- **λ:** The radioactive decay constant (expressed in s^{-1}, min^{-1}, or $year^{-1}$).
- ***N:*** The number of nuclei present at time t.

By integrating this expression from $t=0$ (where $N=N_0$) to time t (where $N=Nt$), we obtain the fundamental law:

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

a. Radioactive Half-life (*T* or *$t_{1/2}$*)

The half-life is the time required for half of the initial quantity of radioactive nuclei to decay. Substituting $N_t = N_0/2$ into the decay law:

$$T = \frac{ln2}{\lambda} = \frac{0.693}{\lambda}$$

After *n* half-lives, the number of remaining nuclei is given by:

$$N_n = \frac{N_0}{2^n}$$

b. Radioactive Activity (*A*) Activity is defined as the average number of disintegrations per unit of time. It is directly proportional to the number of atoms present:

$$A(t) = -\frac{dN}{dt} = \lambda N$$

Units: The SI unit is the **Becquerel (Bq)** (1 disintegration per second). A common historical unit is the **Curie (Ci)** (1 Ci = 3.7×10^{10} dps), based on the activity of 1 gram of Radium-226.

III.4 Applications of Radioactivity

III.4.1 Industrial Applications

Radioactivity is widely utilized in non-destructive testing and quality control:

- **Gammagraphy:** Similar to medical X-rays, gamma radiation (from sources like ^{60}Co or ^{192}Ir) is used to inspect metal parts and welds for internal defects. It is highly valued for its portability and autonomy.
- **Betagraphy:** Utilizing β^- radiation, this technique is employed to measure the thickness of thin materials (like paper or plastic films) during production.

III.4.2 Medical Applications

- **Radiotherapy:** Focused radiation is used to destroy cancerous cells.
- **Medical Imaging:** Radioactive tracers allow for the visualization of organ function (e.g., Technetium-99m).

Chapter VI

Electronic structure of the atom

We now know that an atom of charge number Z is made up of a mass-consistent nucleus containing Z protons and (A-Z) neutrons and Z e(-)s, which ensure the neutrality of the atom. How are the e- located in relation to this nucleus?

VI-1 Introduction to early atomic models

VI-1-1 Thomson's model

The atom is depicted as a sphere composed of positively charged matter, with electrons embedded within it to maintain overall neutrality.

However, this model is completely inaccurate as it fails to account for the presence of the nucleus and the empty space that exists within an atom.

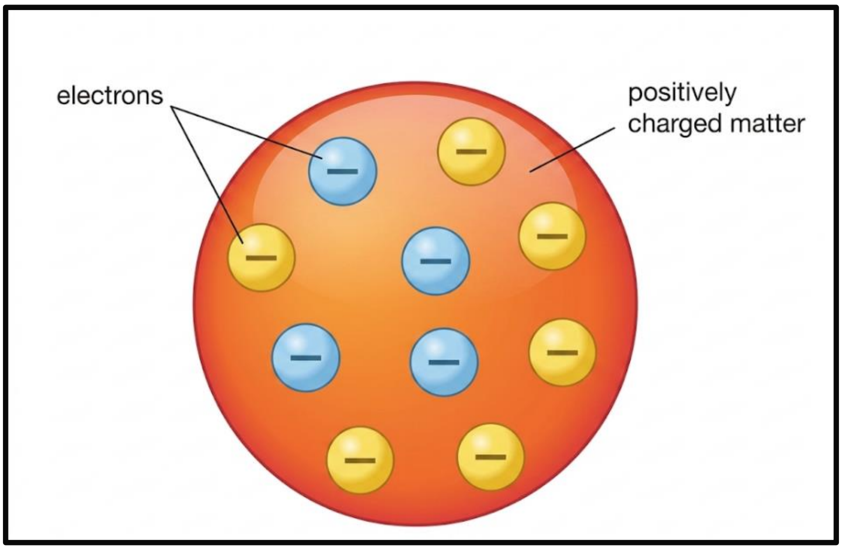


Figure 12. J.J. Thomson’s Atomic Model (1904)

VI-1-2 Rutherford model

This model is based on the existence of the nucleus, in which virtually all the atom's mass is concentrated, and around which electrons gravitate.

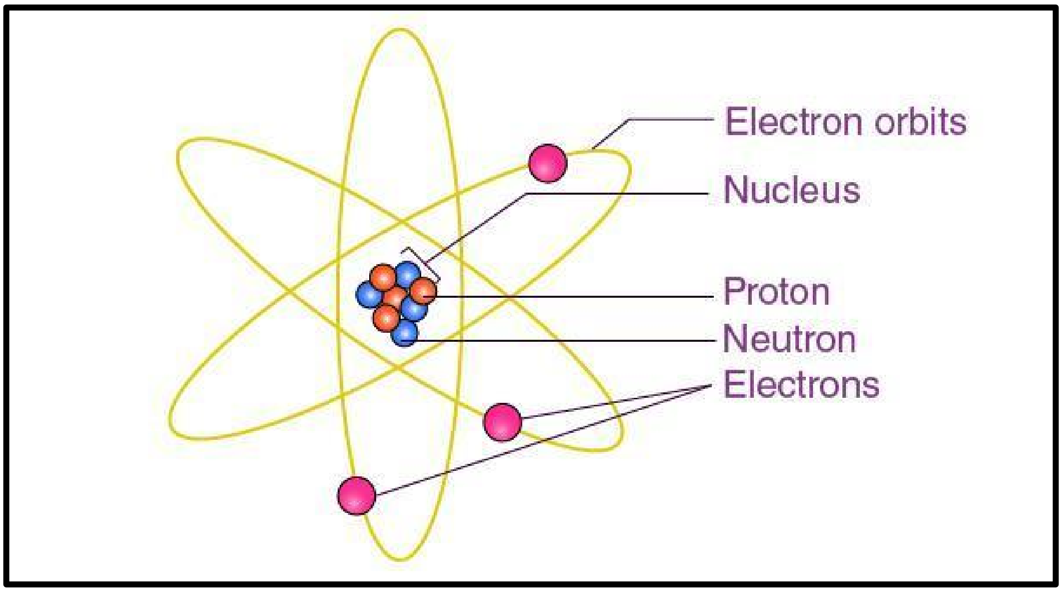


Figure 13. The Rutherford-Bohr Planetary Model of the Atom

Mechanical stability results from the compensation of attractive forces (F1) by centrifugal forces (F2) due to the rotation of electrons around the nucleus. The advantage of this model is that it appeals only to the laws of classical mechanics. On the other hand, it has its weaknesses:

Limitations of Rutherford Atomic Mode :

While Rutherford's atomic model was derived from experimental observations, it was unable to explain certain aspects of atomic behavior.

- Rutherford proposed that electrons travel around the nucleus in fixed circular paths known as orbits. However, Maxwell's theory states that an accelerating charged particle emits electromagnetic radiation. Consequently, an electron moving in an orbit should continuously release energy in the form of radiation. This energy loss would gradually reduce the size of the orbit, causing the electron to spiral inward and eventually collapse into the nucleus. As a result, the model contradicted Maxwell's theory and failed to explain why atoms remain stable.

- Another major limitation of Rutherford's model was its lack of explanation regarding the specific arrangement of electrons within an atom, making the theory incomplete.
- Despite their inaccuracies and inability to account for certain experimental findings, early atomic models provided the foundation for further advancements in quantum mechanics.
- Electromagnetic theory requires the electron to radiate electromagnetic waves, so it will lose energy and eventually fall onto the nucleus.
- The light energy emitted varies continuously, so the spectrum is continuous.

Experimental results show that :

1- The atom exists and does not destroy itself

2- The emission spectrum of any body is a non-continuous spectrum.

The ***electromagnetic spectrum*** encompasses the complete ***range of wavelengths*** associated with all forms of electromagnetic radiation. It consists of various types of radiation, including gamma rays, X-rays, ultraviolet, visible light, infrared, and others.

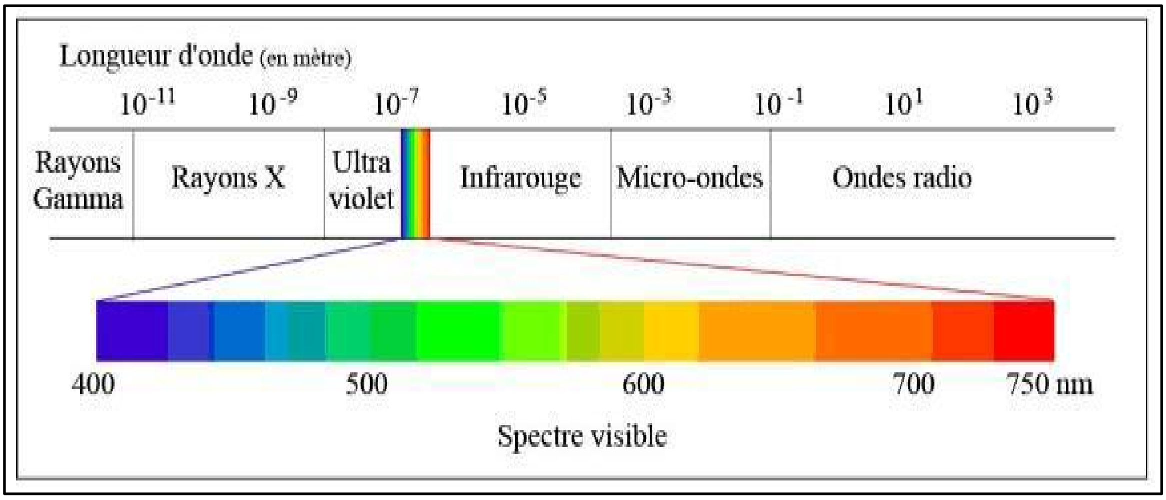


Figure 14. Diagram of the electromagnetic spectrum.

VI-2 Bohr model (Case of the hydrogen atom)

Bohr refined Rutherford’s atomic model by addressing its limitations.

A) To prevent electrons from continuously losing energy and collapsing into the nucleus, he proposed that electrons remain in fixed orbits with specific energy levels.

B) To account for the discrete nature of atomic spectra, he introduced the concept of well-defined energy levels.

In this model, electrons move around the nucleus in ***quantized orbits***, meaning they can only exist at ***specific energy*** levels (designated by the principal quantum number, n).

Bohr's postulates:

A postulate is a fundamental assumption that cannot be proven but is essential for constructing a logical demonstration or theoretical framework. The Bohr model of the atom is based on four key postulates, which describe the behavior of electrons in discrete orbits around the nucleus, ensuring the stability of atomic structure and energy quantization.

VI.2.1 Bohr's First Postulate: The first postulate states that an atom consists of a dense central core called the ***nucleus***, which contains all the ***protons*** and ***neutrons***. Despite its significant mass, the nucleus is extremely small in size. Within the atom, the nucleus remains fixed in position, while an ***electron***, possessing a ***mass*** m, revolves around it in a ***circular orbit*** of radius r.

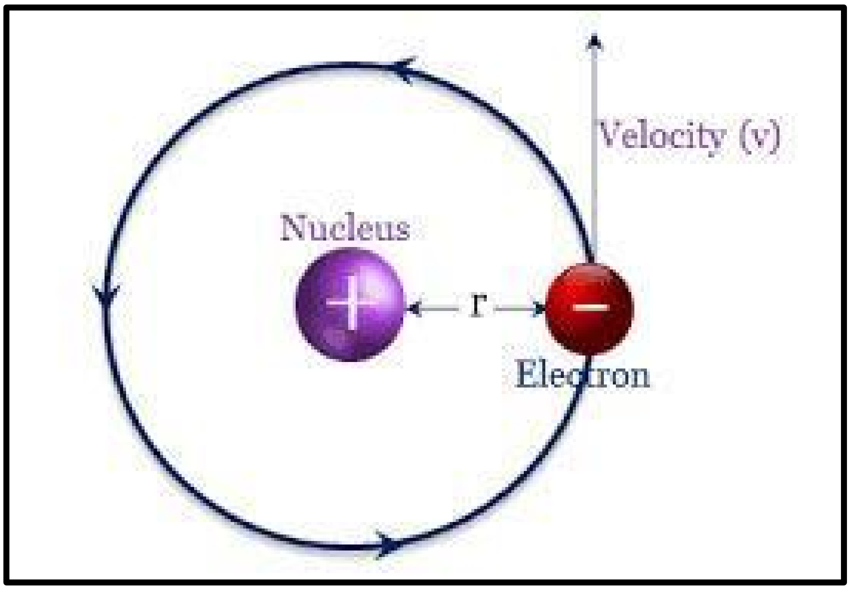


Figure 15. Atomic Orbital Parameters (r, v)

VI.2.2 Bohr's Second Postulate:

The second postulate states that within an atom, The electron in an atom moves around the nucleus in specific, discrete orbits, referred to as stationary or stable orbits. Within these privileged orbits, the electron does not emit energy, maintaining a constant energy level. These stationary orbits form a discontinuous set, ensuring that no radiation is emitted as long as the electron remains in a given orbit.

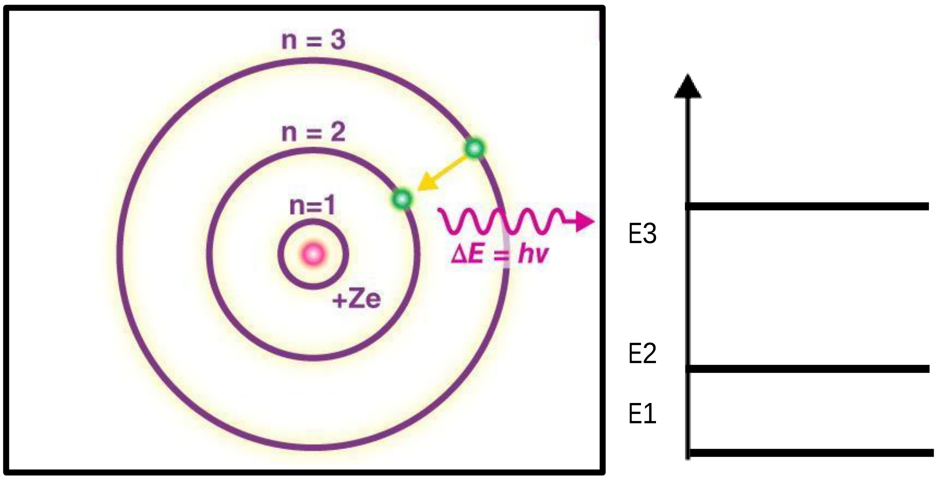
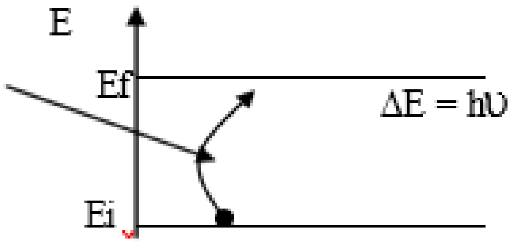


Figure 16. Quantized Electron Shells and Energy Levels

VI.2.3 Bohr's Third Postulate: The third postulate states that when an electron transitions between two energy levels, from an initial orbit n_1 to a final orbit n_2 (where $n_2 > n_1$), it either ***absorbs*** or ***emits*** energy. This energy change is given by the equation:



$$\Delta E = E_f - E_i = h\upsilon \quad \text{or} \quad \Delta E = E_{n_2} - E_{n_1} = h\upsilon$$

ΔE: energy quantity = electromagnetic photon = electromagnetic radiation.

h: Planck constant ($h = 6.62\ 10^{-34}$ J s)

υ: Frequency **$\upsilon = C/\lambda$,** where: C is the speed of light in a vacuum (3×10^8 m/s),

λ : is the wavelength of the emitted or absorbed radiation.

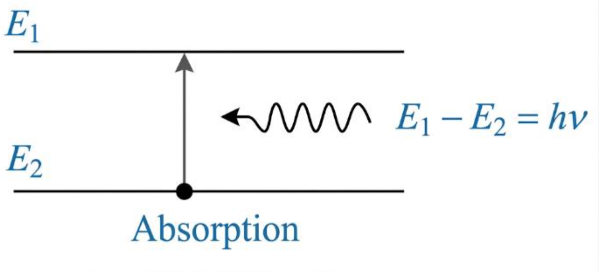
Additionally, the stability of the electron’s motion is maintained by the balance between two forces: the electrostatic force of attraction exerted by the nucleus and the centrifugal force due to the electron’s circular motion. This equilibrium ensures the electron remains in its designated orbit.

Force of attraction towards nucleus = centrifugal force

The atom emits or absorbs radiation when an electron transitions between discrete energy levels, moving from one stationary orbit to another.

the emission or absorption of radiation occurs as a discrete quantum (photon), with energy $\boldsymbol{h\nu}$ corresponding precisely to the energy difference $\boldsymbol{\Delta E}$ between the electron's initial and final orbitals. Consequently, the relationship is expressed as $\boldsymbol{h\nu=\Delta E}$.

a) Absorption:

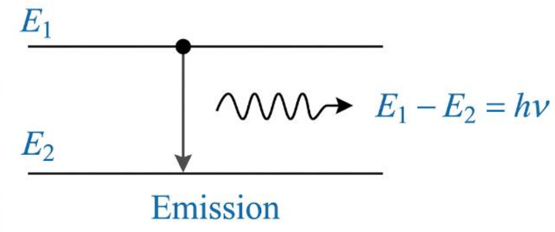


$\Delta E = E_f - E_i = E_{n2} - E_{n1}$

$\Delta E_{abs} = \boldsymbol{h\upsilon > 0}$

b) Emission:

$\Delta E = E_f - E_i = E_{n1} - E_{n2}$



$\Delta E_{emi} = \boldsymbol{h\upsilon < 0}$

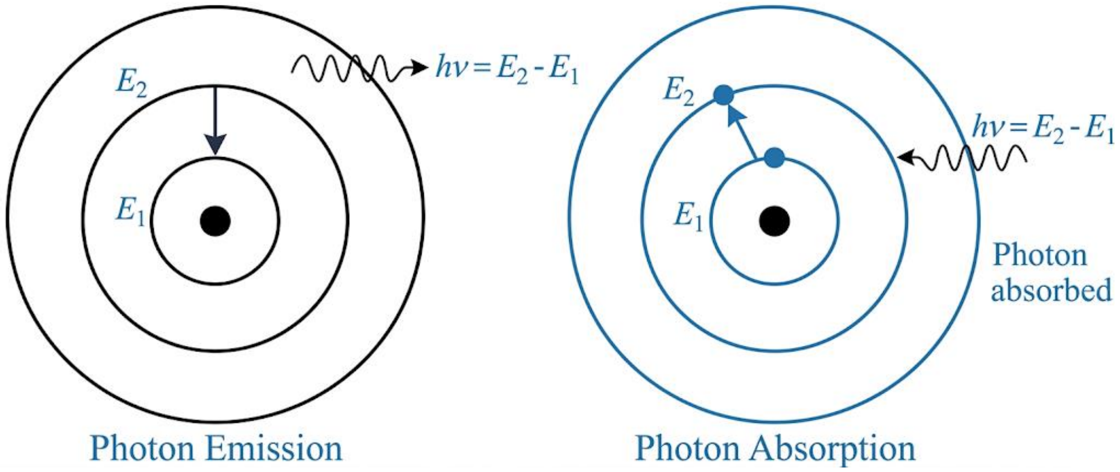


Figure 17. Schematic of Electronic Transitions and Energy Differential (ΔE)

VI.2.4. Bohr's Fourth Postulate:

An electron can only occupy specific allowed orbits where its **angular momentum** (mvr) is a whole-number multiple of $h/2\pi$.

This means that the allowed electron orbits are those in which the product of the electron’s mass, velocity, and orbital radius (r) corresponds to an integer multiple of the reduced Planck’s constant, ħ (where ħ = h/2π)..

$$mv_n r_n = \frac{nh}{2\pi} \quad \text{or} \quad mvr = n\,\hbar$$

h: Planck's constant.

n: Principal quantum number (n = 1, 2, 3,……).

m: Mass of the electron.

r_n : Radius of the nth orbit.

v_n: speed of the electro in the nth orbit.

VI.2.5 Results of Bohr's Postulates

a)- The Bohr radius (r_n) :

The radius of a given orbit n for the Hydrogen atom is:

$$r_n = a_0 n^2$$

. Where a_0 (Bohr radius) = 0.53 = Å (0.53 x 10^{-10} m).

- **n = 1**: Ground state (most stable, lowest energy).

Calculate radius for n=1, 2, 3 :

- **For n=1**: $r_1 = 0.53 \times 1^2 = 0.53$ Å
- **For n=2**: $r_2 = 0.53 \times 2^2 = 2.12$ Å

- **For n=3**: $r_3 = 0.53 \times 3^2 = 4.77$ Å

b)- Electron Velocity in Orbit (v_n):

From Bohr's 4th postulate (quantization of angular momentum) and the balance between electrostatic and centripetal forces, the velocity of an electron in a given orbit *n* is derived as follows:

For a hydrogen-like atom (hydrogenoid), the velocity is:

$$V_n = \frac{2\,\pi\,K\,e^2\,Z}{n\,h}$$

Where:

- Z: Atomic number.
- e: Elementary charge.
- k: Coulomb constant.
- n: Principal quantum number.
- h: Planck's constant.

Alternatively, the relationship between velocity, radius, and mass is expressed by

$$v_n = (k \,.\, Z.\, e^2/m\,.r_n)^{1/2}$$

Numerical Application for the Hydrogen Atom (Z=1):

In the CGS system, the velocity is often simplified to:

$$V_n = 2.188 \times 10^8 / n \quad (cm.\ sec^{-1})$$

c)- Orbital Energy (E_n) :

The energy of an electron in orbit *n* is quantized:

$$\boldsymbol{E_n = \frac{E_1}{n^2} = \frac{-13.6\ eV}{n^2}}$$

- .The principal quantum number n ϵ N designates the orbit.

VI.3 Transition Energy and Balmer's formula: from the 3rd postulate we have :

According to Bohr's 3rd postulate, when an electron jumps from an outer orbit (n_2, higher energy) to an inner orbit (n_1, lower energy), radiation is emitted:

$$\Delta E = E_{n1} - E_{n2} = h\nu = \frac{h\nu}{\lambda}$$

VI.4 The Rydberg Formula (Balmer's Relation) :

$$\bar{\upsilon} = \boldsymbol{\frac{1}{\lambda} = RH \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

- R_H (Rydberg constant) = 1.1 $\times 10^7$ m^{-1}
- $\bar{\upsilon}$: Wavenumber.

$$\Delta E = E_{n1} - E_{n2} = \frac{2\,\pi^2\,k^2 m e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \Delta E = 13.6\,\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

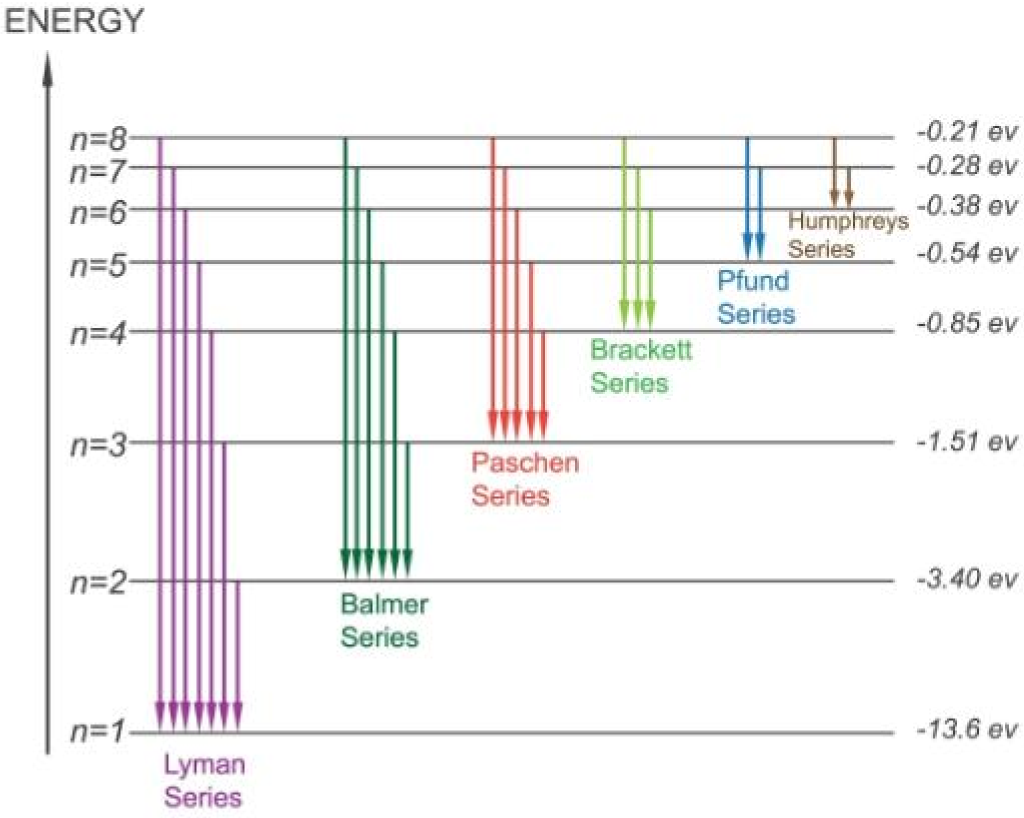


Figure 18: Line spectrum of Hydrogen atom.

Table 6 . Electronic Transition Series and Spectral Regions

Series	n_1 (Final)	n_2 (Initial)	Spectrum Region
Lyman	1	2, 3, ...	Ultraviolet (UV)
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	Infrared (IR)
Brackett	4	5, 6, ...	Near Infrared
Pfund	5	6, 7, ...	Far Infrared

VI.5 Generalization to Hydrogen-like Ions (Hydrogenoids)

Bohr's theory is applicable to hydrogen and hydrogen oxide , A **hydrogenoid** is an ion containing only one electron (e.g., He^+, Li^{2+}).

- ✓ **Radius**: $r_{n\,Z} = \frac{a_0\,n^2}{Z}$
- ✓ **Energy**: $E_{n\,Z} = \frac{-13.6\quad Z^2}{n^2}$
- ✓ **Wavenumber**:

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

- ✓ **Ground State, Excited States, and Ionization**

- **n=1**: Ground state (most stable).
- **n > 1**: Excited states (E > -13.6 eV).
- **n = ꝏ:** The electron is removed from the atom ($E_\infty = 0$).

- ✓ **Ionization Energy (E_i):**

The energy required to extract the electron to infinity:

$$\Delta E = E_{\infty} - E_{n2} \quad (E_i > 0)$$

- For Hydrogen: E_i = 0 - (-13.6) = **+13.6 eV**.

VI.6 Modern Theory: Quantum Mechanics

Bohr's theory failed for multi-electron atoms. Modern theory treats the electron as both a particle and a wave **(Wave-Particle Duality).**

De Broglie Relation :

$$\lambda = \frac{h}{mv}$$

This theory was able to explain the state of e- in atoms. The e(-) is a corpuscle of mass (m) that moves in a wave-like fashion, its wavelength given by the "De BROGLIE" relation.

Planck's constant: h = 6.62 10 - 34J.

The Atomic Orbital (AO): An electron is no longer seen as being on a fixed "track" (orbit), but rather in a volume of space called an **orbital**, where the probability of finding the electron is high.

VI.7 The Four Quantum Numbers

1. **Principal (n)**: $n \in \{1,2,\dots,\infty\}$. Defines the shell *(K,L,M…)* and energy level.

2. **Secondary/Azimuthal (l)**: $0 \leq l \leq n-1$. Defines the subshell shape (*s,p,d,f*).
    - $l=0 \rightarrow s$
    - $l=1 \rightarrow p$
    - $l=2 \rightarrow d$
    - $l=3 \rightarrow f$
3. **Magnetic** ***(m_l)***: $-l \leq m_l \leq +l$. Defines the orientation of the orbital in space.
4. **Spin (*s*)**: $s = \pm 1/2$. Defines the rotation (spin) of the electron.

- **Subshell *s*** *(l=0)* : 1 orbital → max **2 electrons**.
- **Subshell *p*** *(l=1)* : 3 orbitals → max **6 electrons**.
- **Subshell *d*** *(l=2)* : 5 orbitals → max **10 electrons**.
- **Subshell *f*** *(l=3)* : 7 orbitals → max **14 electrons**.**7.2**

VI.8 Graphical Representation of Wave Functions $\Psi_{n,l,m}$

In quantum mechanics, the square of the wave function Ψ^2 represents the probability density of finding an electron in a specific region of space. The volume of space where this probability is high (typically >90%) is called an **Atomic Orbital (AO)**.

VI.8.1 Description of "s" Orbitals

The **s orbital** is defined by the angular quantum number $l = 0$, which implies the magnetic quantum number $m = 0$.

- **Wave Function Symbol:** $\boldsymbol{\Psi}_{n,0,0}$
- **Symmetry:** It possesses **spherical symmetry**, meaning the probability of finding the electron depends only on the distance r from the nucleus, regardless of the direction.
- **Evolution:** As the principal quantum number n increases (*1s, 2s, 3s* ….) the size of the sphere increases.

VI.8.2 Description of "p" Orbitals

The **p orbitals** are defined by $\boldsymbol{l = 1}$, which allows for three possible values of the magnetic quantum number: $\boldsymbol{m = -1, 0, +1}$.

- **Shape:** These orbitals are "dumbbell-shaped," consisting of two lobes separated by a nodal plane (where the probability of finding an electron is zero).
- **Orientations:** The three orbitals are mutually perpendicular and oriented along the Cartesian axes:
  - $\boldsymbol{\Psi(n, 1, 0)}$ or $\boldsymbol{np_z}$: Oriented along the z-axis.
  - $\boldsymbol{\Psi(n, 1, -1)}$ or $\boldsymbol{np_x}$: Oriented along the x-axis.
  - $\boldsymbol{\Psi(n, 1, +1)}$ or $\boldsymbol{np_y}$: Oriented along the y-axis.

Example: For the *n=2* shell, the *2p* subshell contains three degenerate orbitals (orbitals of equal energy): *2px, 2py,* and *2pz.*

VI.8.3 Description of "d" Orbitals (For Reference)

The **d orbitals** are defined by **l = 2**, implying five 5 possible orientations (***m* = *-2, -1, 0, +1, +2***).

- **Conditions:** These orbitals only appear starting from the M layer (**n3**).
- **Shape:** Their geometry is more complex (Figure), typically featuring four lobes (cloverleaf shape), except for the dz^2 orbital, which has a unique "doughnut" shape around its center.

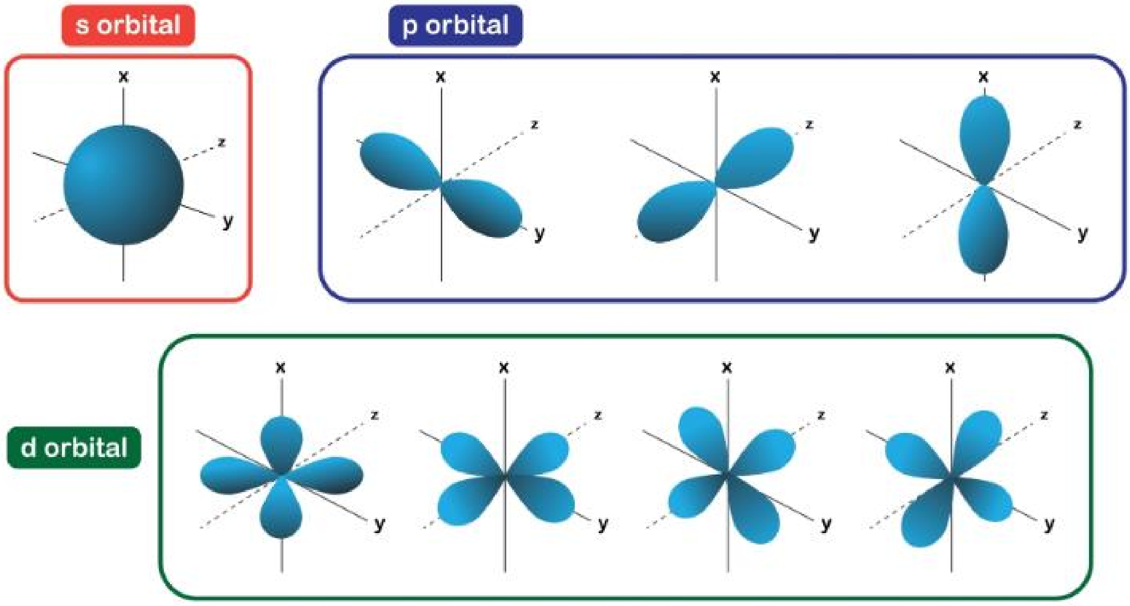


Figure 19: The shapes of atomic orbital

VI.9 Electronic structure of atoms (electronic configuration)

The electronic configuration of an atom is the distribution of its Z electrons among the atomic orbitals (AOs) in the ground state. These orbitals are filled according to four fundamental rules.

VI.9.1 Rules for filling atomic orbitals

a) Klechkowski's Rule (or energy order , The *n* + *l* Rule)

- **Energy Order:** Orbitals are filled in increasing order of the sum ($n + l$). The lower the value of ($n + l$), the lower the energy.
- **Tie-breaking Rule:** If two subshells have the same ($n + l$) value, the one with the **smaller n** has the lower energy and is filled first.
- **Notation:** Electrons are indicated as superscripts (e.g., $1s^2$, $3p^6$).

  This energetic order of atomic orbitals follows a progression that can be represented by the Klechkowski (or energy) diagram:
- **The Klechkowski diagram :**

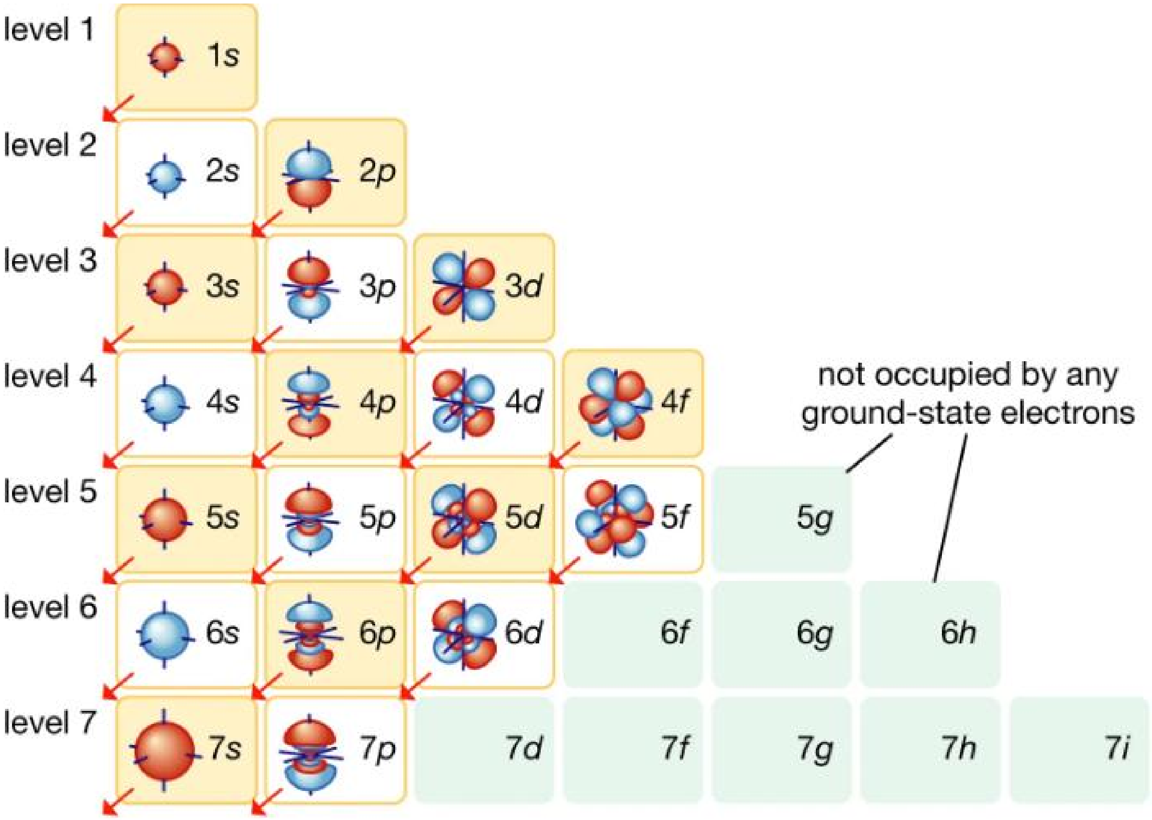


Figure 20. Klechkowski's diagram

Example: the electronic sequence of elements will be :

$_{9}$**F:** $1s^2 / 2s^2\ 2p^5$

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

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

b) Pauli Exclusion Principle

It is impossible for two electrons in the same atom to have the same four quantum numbers *(n, l, m_l, s)*. Consequently, an orbital can hold a maximum of two electrons, which must have opposite spins.

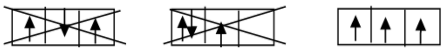
Example for $1s^2$:

Electron 1: *n*=1, *l*=0, *m*=0, s= +1/2 (↑)

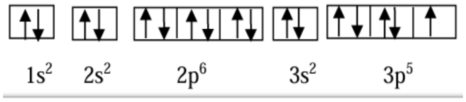
Electron 2: *n*=1, *l*=0, *m*=0, s= -1/2 (↓)

c) Hund’s Rule (Maximum Multiplicity)

For degenerate orbitals (*p*, *d*, *f*), filling must proceed by placing one electron in each orbital with parallel spins before pairing them.



Exemple : $_{17}$Cl : $_{20}$Ca: $1s^2$ / $2s^2$ $2p^6$ / $3s^2$ $3p^5$



VI.9.2 Electronic structure of atoms

The electronic structure of atoms is expressed as :

a) Filling Pattern

Filling is carried following Klechkowski’s order exactly:

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

$_{36}$Kr: $1s^2$ / $2s^2$ $2p^6$ / $3s^2$ $3p^6$ / $4s^2$ $3d^{10}$ $4p^6$

b) Final Electronic Configuration (Ranking by *n*)

To represent the physical structure (distance from the nucleus), we reorder the subshells by the principal quantum number *n*.

- **Step 1:** Establish the sequence via Klechkowski.
- **Step 2:** Rectify the order of n (ascending).
- **Example of $_{26}$Fe:**

- *Filling order:* ... $3s^2\ 3p^6\ 4s^2\ 3d^6$
- *Final Configuration:* $1s^2$ / $2s^2\ 2p^6$ / $3s^2\ 3p^6$ / $4s^2\ 3d^6$

VI.9.3 Valence and Core Electrons

1. **Core Electrons:** Electrons belonging to the previous Noble Gas. They are stable and do not participate in chemical reactions.
2. **Valence Electrons:** Electrons located outside the Noble Gas core. They are involved in chemical bonding.
    - **Note:** Saturated d^{10} or f^{14} subshells are considered part of the core.

- **Example:**
- **$_{26}$Fe :** [$_{18}$Ar] $4s^2\ 4d^6$
    - *Core:* 18 (Ar) = 18 electrons.
    - *Valence:* $4s^2\ 4p^6$ = 8 electrons
- **$_{35}$Br:** [$_{18}$Ar] $3d^{10}\ 4s^2\ 4p^5$
    - *Core:* 18 (Ar) + 10 ($3d^{10}$) = 28 electrons.
    - *Valence:* $4s^2\ 4p^5$ = 7 electrons.

VI.9.4 Valence Shell and Subshells (s/c)

- **External Valence Subshells:** The *ns* and *np* subshells with the highest *n*. These electrons are typically lost first during ionization.
- **Internal Valence Subshells:** Partially filled *(n-1)d* or *(n-2)f* subshells.
- **Valence Shell:** The shell with the largest *n* value.
- **Example :**

$_{53}$**I:** [$_{36}$Kr] $4d^{10}\ 5s^2\ 5p^5$

- Valence shell: *n=5*
- External valence: *5s and 5p*

VI.9.5 Chemical Valence (Valency)

The valency of an element is defined by the number of **unpaired electrons** present in the atom in its ground state. This number determines the atom's capacity to form chemical bonds.

- $_8$**O**: $1s^2$ / $2s^2\ 2p^4$ → (↑↓) (↑↓) (↑) (↑) → **2 unpaired electrons = Divalent.**
- $_{11}$**Na:** $1s^2$ / $2s^2\ 2p^6$ / $3s^1$ → (↑) → **1 unpaired electron = Monovalent.**
- $_7$**N:** $1s^2$ / $2s^2\ 2p^3$ → (↑↓) (↑) (↑) (↑) → **3 unpaired electrons = Trivalent.**

VI.9.6 Magnetic Properties of Elements

The magnetic behavior of an atom depends on the presence or absence of unpaired electrons:

a) Diamagnetic Elements

Atoms in which all electrons are paired (with opposite spins). They lack a permanent magnetic moment and are very weakly repelled by a magnetic field.

- *Examples:*($_2$He: $1s^2\ 2s^2$),($_4$Be: $1s^2\ 2s^2$), $_{30}$Zn([Ar] $4s^2\ 3d^{10}$**) .**

b) Paramagnetic Elements

Atoms possessing one or more unpaired electrons. They have a net magnetic moment and are attracted to a magnetic field.

- *Examples:*(${}_1$H: $1s^1$) ,(${}_3$Li: [He] $1s^2$ $2s^1$), ${}_{26}$Fe([Ar] $4s^2$ $3d^6$**) .**

VI.10 Screening Effect: Slater's Approximation

Slater's rules provide a semi-empirical method to calculate the shielding constant ($\boldsymbol{\sigma}$) and the effective nuclear charge (Z^*) using the formula:

$$Z^* = Z - \boldsymbol{\sigma}$$

Where: **Z**: Real nuclear charge (atomic number). $\boldsymbol{\sigma}$: Screening constant.

To determine the effective charge, follow these steps:

- ✓ Write and properly order the element's configuration into specific groups.
- ✓ Identify the target electron for which $Z^*$is being calculated.
- ✓ Contribution: Every other electron contributes a partial screening value $\boldsymbol{\sigma_i}$ to the total constant $\boldsymbol{\sigma}$, depending on:
  - The orbital type (s, p, d, or f).
  - The electronic shell (n) where the electron resides.

The values of $\boldsymbol{\sigma_i}$ are summarized in the following table:

Group of the electron (E)	Other electrons in the same group	Electrons in shell (n−1)	Electrons in shells (n−2,n−3…)
(*ns,np*)	0.35 (0.30 for 1s)	0.85	1
(nd) or *(nf)*	0.35	1	1

Example: Calculating Z^* for a valence electron in Oxygen ($Z=8$):

- ✓ Configuration: $1s^2$ \ $2s^2$ $2p^4$
- ✓ $\boldsymbol{\sigma}$ = (5 electrons in same shell x 0.35) + (2 electrons in n-1 shell x 0.85)
- ✓ $\boldsymbol{\sigma}$ = 1.75 + 1.70 = 3.45
- ✓ Z^* = 8 - 3.45 = 4.55

Chapter V

Periodic Classification of Elements.

Introduction:

In the 19th century, chemists sought to classify chemical elements based on their atomic weights. However, it was Dmitri Mendeleev’s 1869 system of classification that achieved the greatest success and enduring influence. Mendeleev arranged the elements into rows and columns according to increasing atomic mass, famously leaving gaps for undiscovered elements and revealing recurring patterns in their properties. While the modern periodic table has since been refined to organize elements by atomic number (Z), Mendeleev's systematic approach remains the foundation for how we identify and interpret the essential characteristics of each element today.

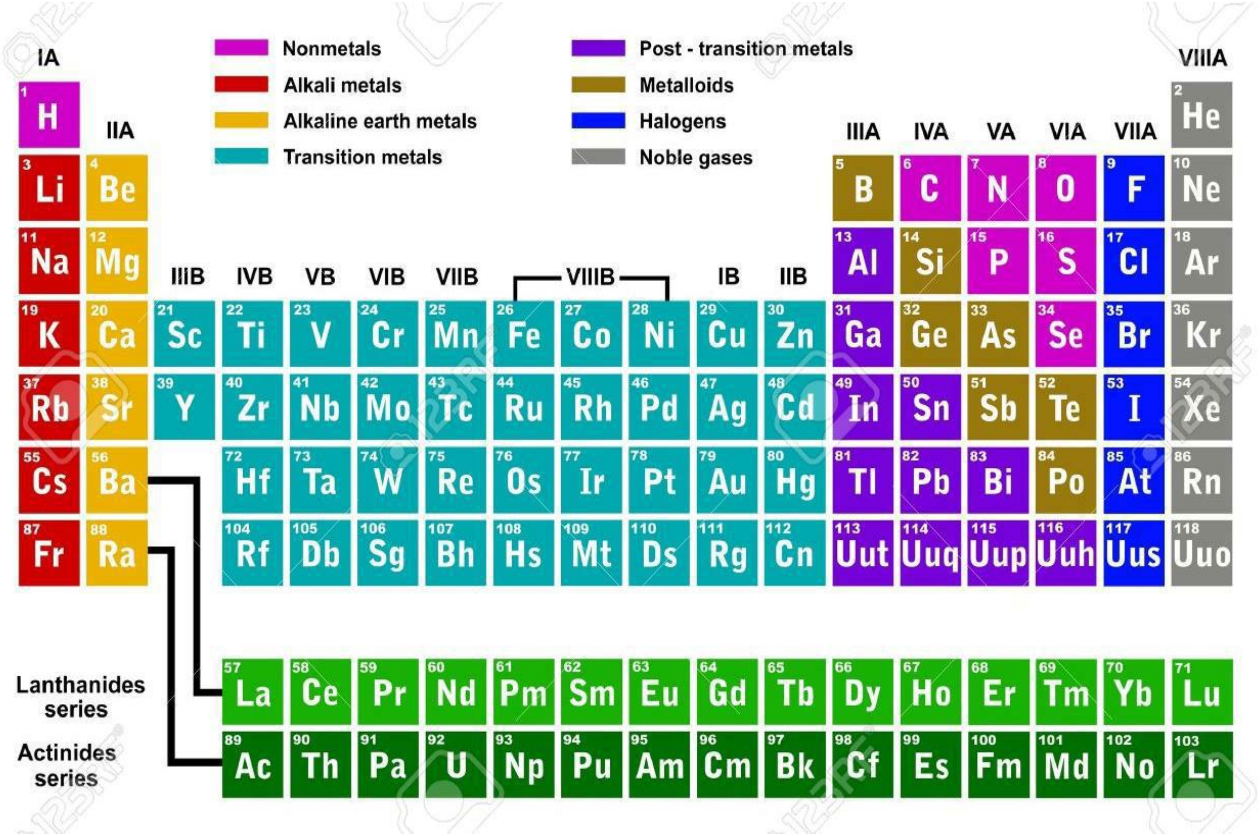


Figure 21. Periodic Table of the chemical elements.

V.1 Mendeleev's Periodic Classification

In Mendeleev's first classification (1869), chemical families were organized according to their **atomic masses**. His true originality lay in leaving certain slots vacant within the table, predicting the existence of then-unknown elements. Similarly, the **electron configuration** of atoms in their ground state allows for the reconstruction of the periodic table—specifically, the distribution of elements into rows (periods) and columns (groups).

V.2 The Modern Periodic Classification

Mendeleev's classification arranged elements in order of increasing atomic mass; however, an element is actually defined by its **atomic number (Z)** rather than its atomic mass, which can vary due to the existence of **isotopes**.

The modern classification is based on the increasing order of Z. This classification is organized into a table consisting of:

- **Seven (7) rows**, known as **periods**.
- **Eighteen (18) columns**, known as **groups** or subgroups.
- The **atomic number** increases from left to right in a **period (row)** and from top to bottom in **groups (column)**.

V.3 Description of the periodic table of elements

The periodic table is organized into a specific grid defined by the electron configuration of the elements. This structure is divided into **periods** and **groups**.

a) Periods (Rows):

The periodic table is divided into seven periods, each corresponding to a principal quantum number (n), which denotes the primary energy level occupied by the valence electrons of the elements within that period. The **1st** period (n = 1) comprises 2 elements, reflecting the capacity of the 1s orbital. The **2nd** and **3rd** periods (n = 2 and n = 3) each contain 8 elements, corresponding to the filling of the 2s and 2p, and 3s and 3p orbitals, respectively. The **4th** and **5th** periods (n = 4 and n = 5) include 18 elements each, as electrons fill the 3d and 4d subshells in addition to the s and p orbitals. The **6th** period (n = 6) also contains 18 elements in its main structure, though it is commonly associated with the lanthanide series (4f block), which are often displayed separately. Finally, the **7th** period (n = 7) encompasses 32 elements, including the actinide series (5f block), which, due to complex electron configurations and the involvement of inner transition metals, contribute to the extended layout of the modern periodic table.

Table 7. Distribution of Elements Across Periodic Table Periods

N	Period	Elements
1	**1st**	2
2	**2nd**	8
3	**3rd**	8
4	**4th**	18
5	**5th**	18
6	**6th**	32
7	**7th**	32

b) Columns (groups)

Groups (columns) in the periodic table consist of elements that share the same external electronic structure, meaning they possess the ***same*** number of valence electrons. The periodic table is organized into **18** columns, corresponding to **8 main groups** traditionally numbered with Roman numerals from **I** to **VIII**, based on the number of valence electrons.

Each group is further divided into subgroups according to the type of atomic orbitals occupied by the valence electrons: in ***subgroup A***, the valence electrons occupy the **s** and/or **p** orbitals, while in ***subgroup B***, they occupy the d orbitals.

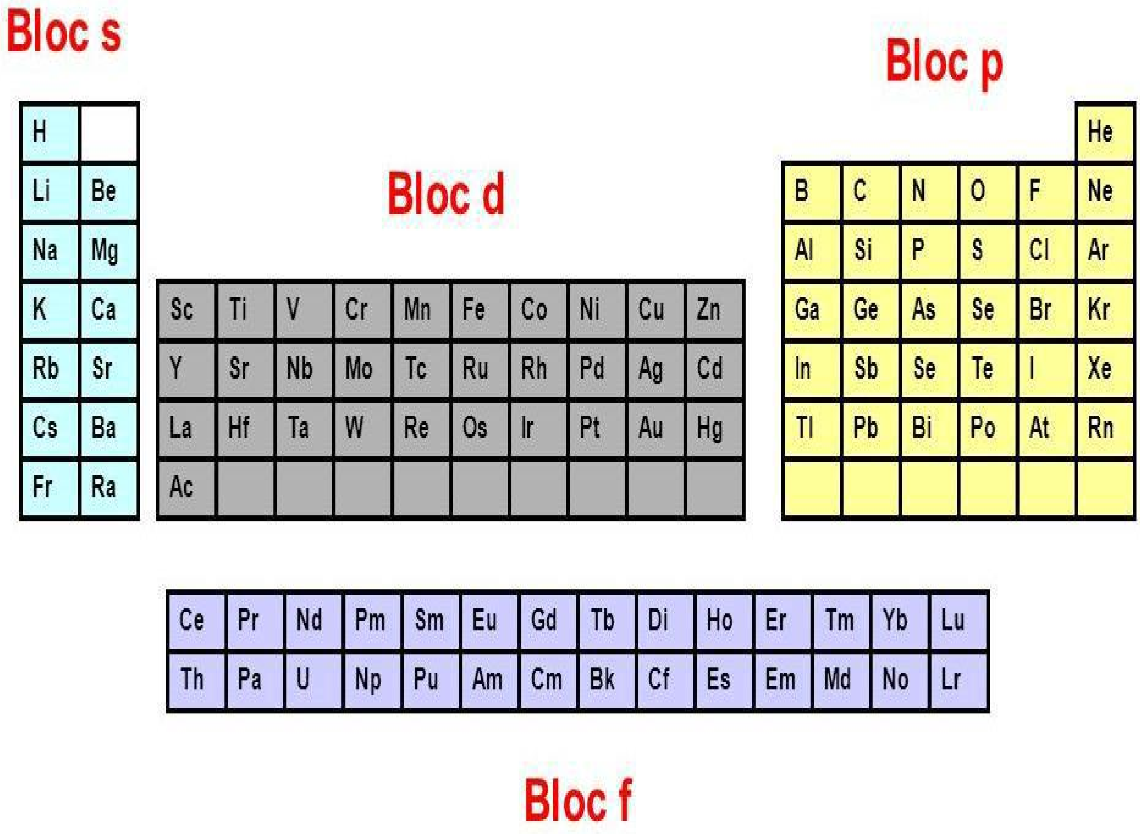


Figure 22. The Blocs (s, p, d and f) on Periodic Table.

c) Blocs

The periodic classification of elements is divided into four blocks based on the external electronic structure: the **s**-block, **p**-block, **d**-block, and **f**-block.

1) **Bloc (s)**:

The **s-block** contains the first two columns (Groups **I** and **II**) of the periodic table.

Group $\mathbf{I_A}$, known as the alkali metals, has an external configuration of $\boldsymbol{ns^1}$, while Group $\mathbf{II_A}$, the alkaline earth metals, has an external configuration of $\boldsymbol{ns^2}$. For instance, lithium (Li, $\boldsymbol{Z=3}$) has the electron configuration $\boldsymbol{[He]2s^1}$, placing it in period **2** and Group $\mathbf{I_A}$; similarly, beryllium (Be, $\boldsymbol{Z=4}$) has $\boldsymbol{[He]2s^2}$, corresponding to period **2** and Group $\mathbf{II_A}$.

Other examples include potassium (K, $\boldsymbol{Z=19}$) with $\boldsymbol{[Ar]4s^1}$ (period **4**, Group $\mathbf{I_A}$) and barium (Ba, $\boldsymbol{Z=56}$) with $\boldsymbol{[Xe]6s^2}$ (period **6**, Group $\mathbf{II_A}$).

2) **Bloc (p)**:

The **p-block** spans six columns (Groups $\mathbf{III_A}$ to $\mathbf{VIII_A}$) with a general external configuration of ns^2np^i (where $\boldsymbol{i}$= **1** to **6**).

This includes Group $\mathbf{III_A}$ ($ns^2np^{\mathbf{1}}$), $\mathbf{IV_A}$ (ns^2np^2), V_A (ns^2np^3), $\mathbf{VI_A}$ (ns^2np^4), $\mathbf{VII_A}$ (ns^2np^5), and $\mathbf{VIII_A}$ (ns^2np^6).

Examples include carbon (**C**, $\boldsymbol{Z=6}$), $[He]2s^{\mathbf{2}}\boldsymbol{2p^2}$ (period 2, Group IV_A), oxygen (**O**, $\boldsymbol{Z=8}$), $[He]2s^22p^4$ (period 2, Group VI_A), and chlorine (**Cl**, $\boldsymbol{Z=17}$), $[Ne]3s^2\boldsymbol{3p^5}$ (period 3, Group VII_A). Notably, for periods $\boldsymbol{n\geq 4}$, p-block elements exhibit a saturated d-subshell ($(n{-}1)d^{10}$, enhancing their stability. For instance, bromine (**Br, $\boldsymbol{Z}$=35**) has the configuration $[Ar]$ $4s^2\boldsymbol{3d^{10}4p^5}$, and polonium (**Po, $\boldsymbol{Z}$=84**) exhibits $[Xe]$ $6s^24f^{14}\boldsymbol{5d^{10}6p}^4$.

3) Bloc (d):

The **d-block** encompasses ten columns (groups 3 to 12, traditionally labeled as B groups) and begins filling from n=4. The valence shell follows $\boldsymbol{ns^2(n{-}1)d^i}$ (where $\boldsymbol{i}$**=1** to **10**).

In this block, Group $\mathbf{III_B}$ corresponds to $ns^2(n{-}1)d^1$, $\mathbf{IV_B}$ to $ns^2(n{-}1)d^2$, and so forth, up to $\mathbf{II_B}$ (column 12) with $ns^2(n{-}1)d^{10}$.

For example, titanium (**Ti, $\boldsymbol{Z}$=22)** has $[Ar]4s^23d^2$ (period 4, Group IV_B), iron (**Fe, $\boldsymbol{Z}$=26**) is $[Ar]4s^23d^6$ (period 4, Group $VIII_B$), and zinc (**Zn, $\boldsymbol{Z}$=30**) is $[Ar]$ $4s^23d^{10}$ (period 4, Group II_B).

4) Bloc (f):

Finally, the **f-block** elements, characterized by the filling of the f-subshells, consist of the **lanthanides** and **actinides**. The lanthanides follow lanthanum (La, **$\boldsymbol{Z}$=57**) and correspond to the filling of the 4f subshell (n=**6**), while the actinides follow actinium (Ac, **$\boldsymbol{Z}$=89**) and correspond to the filling of the 5f subshell (n=**7**). All actinides are radioactive. The f-block elements are classified as **inner transition** metals and are noted for their incomplete f-orbitals. Moreover, elements with atomic numbers greater than 92, known as **transuranic elements**, are artificial and typically synthesized in nuclear reactors, with plutonium being a notable exception as a naturally occurring element.

V.4 Study of family’s elements of the periodic table

The elements of the periodic table are classified into several categories based on their shared physical and chemical properties. These categories include **alkali metals**, **alkaline earth metals**, **transition metals**, **post-transition metals**, **metalloids**, **halogens**, **noble gases**, and other **non-metals**. Here is a periodic table representing these categories:

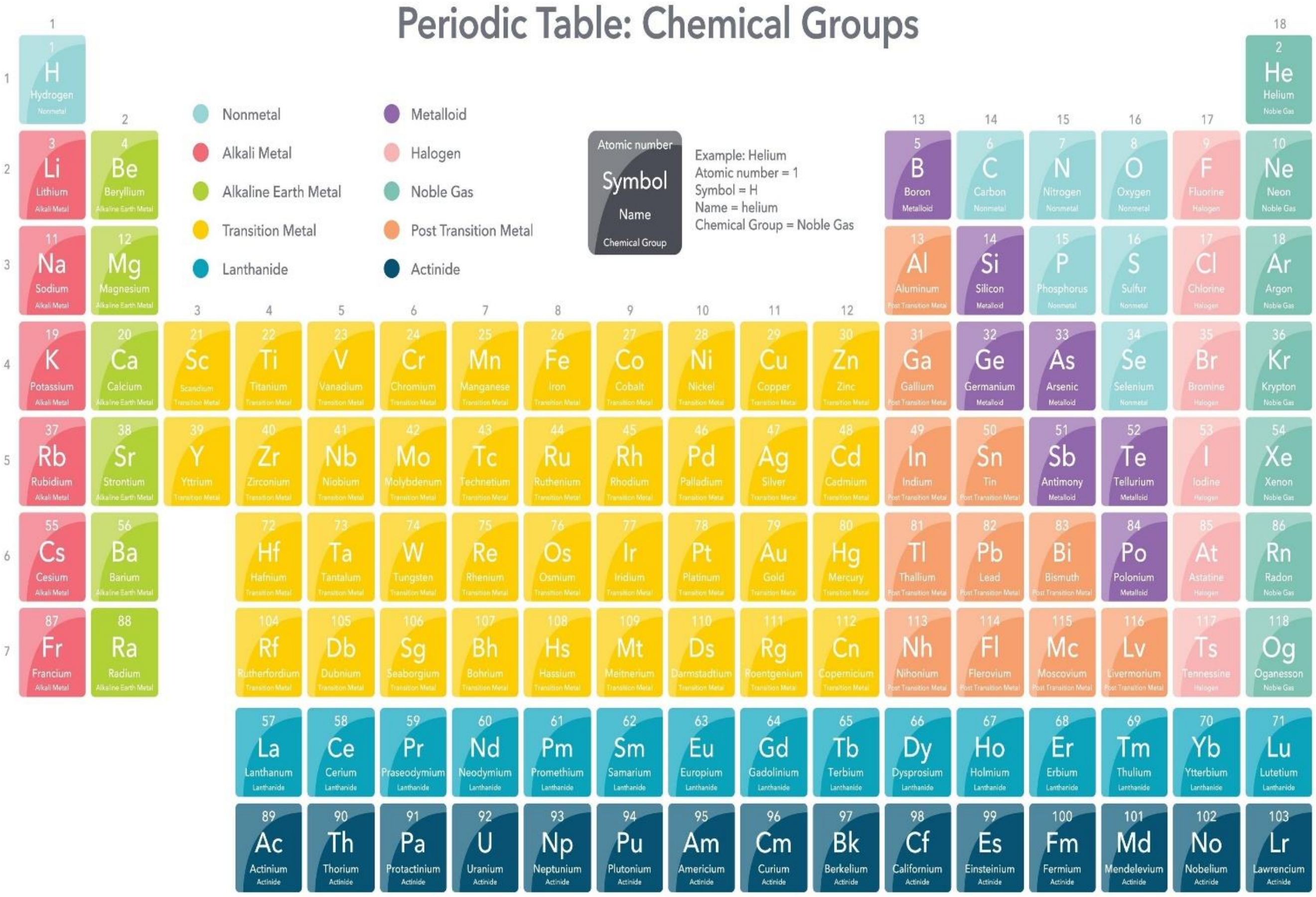


Figure 23. Family’s elements of the periodic table

V.4.1 Metals:

Metals are located at the left and center of the periodic table: They include the **s-blocks** (except hydrogen), the d-block, the f-block and one half of the p-block.

Most elements on the periodic table are metals. Chemically , metals tend to lose electrons to become positive ions (cations); therefore, they are described as electropositive.

K →K+ + 1e- ; Other examples : Fe^{2+}, Ag^{+} , Zn^{2+} .

The elements in the d-block d are the outer transition metals, while the elements in the f-block are known as inner transition metals (**lanthanides** and **actinides**).

V.4.2 Post-transition metals:

Post-transition metals are located in the periodic table, between the transition metals to their left and the metalloids to their right. These metals are typically soft or brittle metals of lower mechanical strength, with lower melting points compared to transition metals. They are : Al, Ga In, Sn, Tl, Pb and Bi

Properties of metals:

- They are typically crystallized solids with high melting points (exception: mercury (Hg) is liquid at room temperature; Gallium (Ga) and Cesium (Cs) have very low melting temperatures).

- the possess high thermal and electrical conductivity.

- The metallic character of the elements increases from top to bottom in a column and from right to left in a period table.

V.4.3 Non-metals:

Non-metals are relatively few in number and they are located on the right of the periodic table (the upper-right portion of the p-block), (e.g.: O, N, C, P), with the exception of hydrogen, which is classified with the a non-metals. They tend to gain electrons and form negative ions (anions) ; and are therefore electronegative.

$$O + 2e^- \rightarrow O^{2-}$$

These categories include:

The **Chalcogens** : the oxygen family (VIA), (Column 16/ Group VIA)

The **halogens** : (Column 17/ Group VIIA), which are highly electronegative.

The **Noble Gases** : (Column 18/ Group VIIIA) , which have a stable configuration (ns^2 np^6) than the rare gas family. These elements are characterized by their high chemical intertness.

V.4.4 Non-metals :

They are gaseous (for the most part), liquid (bromine) or solid (carbon, sulfur) at ordinary temperature. They are at room temperature, most are gases (e.g., N_2, O_2, F_2), one is liquid (Bromine , Br_2), and others are solids (e.g., Carbon, Sulfur, Phosphorus).

Non-metal are generally poor conductors of heat and electricity, except for carbon, which is insulating (diamond) or conductive (graphite).

V.4.5 Metalloids

Mettaloids are found between metals and non-metals, their behavior is both non-metallic and metallic , they possessing some metallic properties (as conducting electricity) and some non-metallic properties. which is ca conduct electricity under specific conditions. They are also known as semiconductors. This class of elements includes boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te) and astatine (At).

V.5 Atomic Characteristics and Periodicity

The properties of elements vary systematically with their position in the periodic table, a phenomenon known as **periodicity**. These properties depend primarily on the effective nuclear charge (Z_{eff}) and the principal quantum number (n).

V.5.1 Atomic Radius (r_a) and Covalent Radius

The atomic radius represents the distance between the center of the nucleus and the outermost electron shell. In the case of non-metals, we often use the **covalent radius**, which is defined as half the distance between the nuclei of two identical atoms joined by a single covalent bond.

- **In a Group (Column):** The atomic radius **increases from top to bottom**. This is due to the increase in the principal quantum number (n), which means more electron shells are added.
- **In a Period (Row):** The atomic radius **decreases from left to right**. As the atomic number (Z) increases, the number of protons increases, leading to a stronger effective nuclear charge (Z_{eff}) that pulls the electrons closer to the nucleus.

V.5.2 Ionic Radius

When an atom becomes an ion, its size changes significantly:

- **Cations (X^+):** The radius of a cation is always **smaller** than its parent neutral atom ($r_{cation} < r_a$). The loss of an electron reduces electron-electron repulsion and often results in the loss of the outermost shell. *Example:* $Na \rightarrow Na^+ + 1e^-$
- **Anions (X^-):** The radius of an anion is always **larger** than its parent neutral atom ($r_{cation} > r_a$). Adding an electron increases electron-electron repulsion, causing the electron cloud to expand. *Example:* $Cl + 1e^- \rightarrow Cl^-$

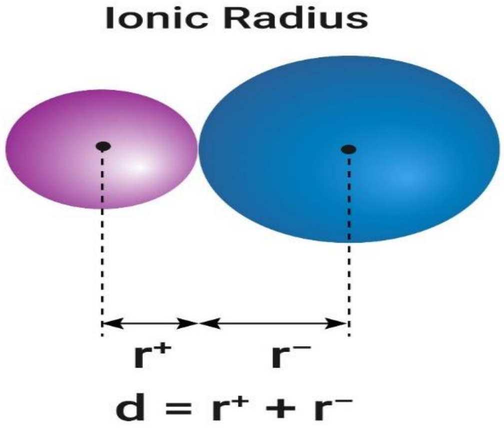


Figure 24: Interatomic Distance (d) as a Function of Ionic Radii (r^+, r^-)

V.5.3 Electronegativity (χ or En)

Electronegativity is a chemical property that measures the tendency of an atom to attract a shared pair of electrons toward itself within a covalent bond.

- **Bond Polarity:** In a bond A—B, if B is more electronegative than A, partial charges appear: $A^{\delta+} — B^{\delta-}$.

Periodic Trends:

- **In a Group:** Electronegativity **increases from bottom to top**.
- **In a Period:** Electronegativity **increases from left to right**.

Scales:

- **Pauling Scale:** The most widely used scale where **Fluorine (F)** is the most electronegative element (value 4.0) and **Cesium (Cs)** or **Francium (Fr)** are the least electronegative.
- **Mulliken Scale:** Based on the average of an element's ionization energy and electron affinity.

V.5.4 Ionization Energy (IE)

Ionization energy is the minimum energy required to remove the most loosely bound electron from an isolated gaseous atom in its ground state to form a cation. Equation:

$$X_{(g)} + IE \rightarrow X^{+}_{(g)} + e^{-}$$

Periodic Trends:

- **In a Group:** IE **decreases from top to bottom**. As the atomic radius increases, the valence electrons are further from the nucleus and are less tightly held.
- **In a Period:** IE **increases from left to right**. As the effective nuclear charge increases and the atomic radius decreases, more energy is required to remove an electron.

It is always harder to remove a second electron than the first (IE1 < IE2 < IE3). A very large jump in energy occurs when an electron is removed from a stable, full-shell (noble gas) configuration.

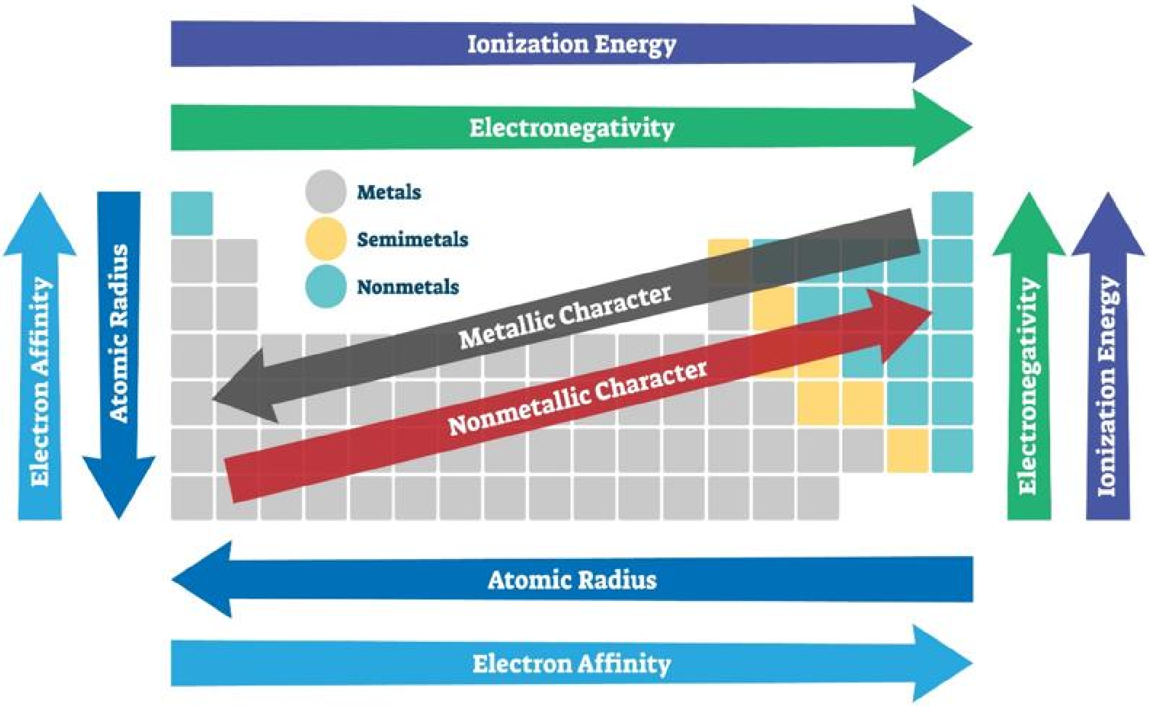


Figure 25. Evolution of Atomic Properties Across Periods and Groups

References

1. R. Ouahès et B. Dévallez, Chimie générale, Editions OPU - Alger, 04 1993.

2. N. Glinka, Chimie générale, tome II, Editions MIR-Moscou, 1981.

3. G. Geiser, G. Delpin et P. Viaud, Chimie générale, Editions DELTA et SPES Lausanne, 1983.

4. F. Houma, Chimie générale, Editions LAMINE - Alger, 1995.

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

6. R. et C. Ouahes, Chimie physique, Ellipses, 1995.

7. M. Gruia, M. Polisset, Chimie générale PCEM, Ellipses, 1993.

8. J.R. Kotz-Treichel, Chimie générale, Editions de boeck, 2006.

9. A. Durupthy, O. Durupthy, 1ière année Chimie PCSI, Hachette Supérieur, 2009.

10. P. Arnaud, Cours de Chimie générale, DUNOD, 2013.

11. http://www.chimie-briere.com.

12. https://programs.usask.ca/

13. https://chem.libretexts.org/

14. https://www.physiquechimiemathbiologie.com