Mohamed Khider University,

Biskra

Faculty of Sciences and

Technology

Course handouts

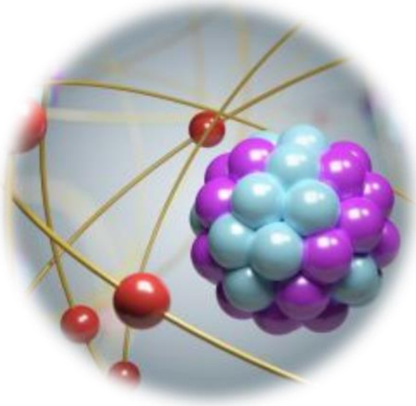
1st year Science and Technology

The Structure of Matter

Realized by

Dr. Sana ALMI

Lecturer class A



Academic year 2021-2022

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CHAPTER 1

FUNDAMENTAL NOTIONS

Chapter contents

- **Macroscopic Characterization and States of the Matter.**
- **Changing States of Matter**
- **Atoms, Elements and Compounds**
- **Mole and Avogadro number**
- **Atomic Mass Unit**
- **Atomic and Molecular Molar Mass, Molar Volume,**
- **Weight Law: Conservation of Mass (Lavoisier).**
- **Chemical Reaction, Qualitative and Quantitative Aspect of Matter.**

CHAPTER 1. FUNDAMENTAL NOTIONS

I- Macroscopic characterization and states of the matter

The physical properties of matter can be viewed from either the macroscopic and microscopic level. The macroscopic level includes anything seen with the naked eye and the microscopic level includes atoms and molecules, things not seen with the naked eye. Both levels describe matter. Matter is anything that occupies space and has mass.

- On the **microscopic level**, chemical symbols represent the behavior of individual atoms and molecules. Atoms and molecules are much too small to be seen, but we can nevertheless describe their microscopic behavior if we read the equation between them.

For example "Two molecules of hydrogen react with one molecule of oxygen to yield two molecules of water." It's often helpful to visualize a molecule as a collection of spheres stuck together.

- On the **macroscopic level**, formulas and equations represent the large-scale behaviors of atoms and molecules that give rise to visible properties. In other words, the symbols and represent not just single molecules but vast numbers of molecules that together have a set of measurable physical properties.

A single isolated molecule is neither solid nor liquid nor gas, but a huge collection of molecules appears to us as a colorless liquid that freezes at 0°C and boils at 100°C. Clearly, it's this macroscopic behavior we deal with in the laboratory when we weigh out specific amounts of reactants, place them in a flask, and observe visible changes.

Moreover, the units of measurement for these properties are also different; for macroscopic properties, the unit of measurement is on a scale that is visible to the naked eye. This includes centi-, kilo-, mega-, etc. For microscopic properties, the unit of measurement is on a scale that is invisible to the naked eye and includes milli-, micro-, nano-, pico-, etc.

Under an international agreement concluded in 1960, scientists throughout the world now use the International System of Units for measurement, abbreviated IS in the macroscopic level of units. Based on the metric system, which is used in all industrialized countries of the world except the United States, the SI system has seven fundamental units (Table 1.1).

Table 1.1. The Seven Fundamental SI Units of Measure

Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Temperature	kelvin	K
Amount of substance	mole	mol
Time	second	s
Electric current	ampere	A
Luminous intensity	candela	cd

Table 1.2.The measurement units for macroscopic and microscopic properties.

Physical Quantity	Unit name	Unit Symbol	Definition
Length	Angstrom	Å	10^{-10}m
	nanometer	nm	10^{-9} m
Area	square meter	m^2	
Volume	cubic meter	m^3	dm^3, 10^{-3} m^3
	liter	ℓ	
	cubic centimeter	cm^3, mℓ	
Mass	atomic mass unit	U(a.m.u)	1.66054×10^{-27} kg
	microgram	µg	10^{-9} kg (10^{-6} g)
Density	Kilogram per cubic meter (IS)	Kg/m^3	
	Gram per milliliter or gram per cubic centimeter	g/mℓ or g/cm^3	
Force	newton	N	kg . m/s^2
Pressure	pascal (SI)	Pa	N/m^2
	bar	bar	10^5 Pa
	atmosphere	atm	101 325 Pa
	torr (millimeter of mercury)	torr (mm Hg)	atm/760 or 133.32 Pa

Exercise 1:

A benzene solution containing 0.10 mm^3 of stearic acid is dropped into a tray full of water. The acid is insoluble in water but spreads on the surface to form a continuous film of area 400 cm^2after all of the benzene has evaporated. What is the average film thickness in (a) nanometers, (b) angstroms?

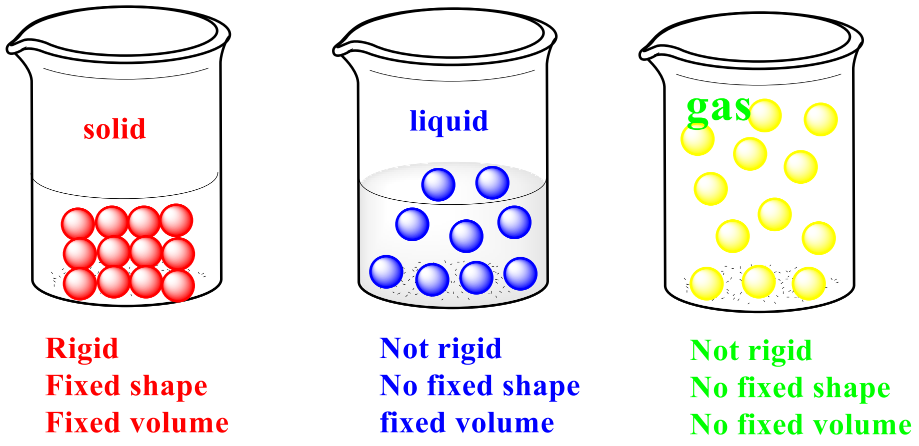
II- Changing states of matter

The state of matter of a substance depends on how fast its particles move and how strong the attraction is between its atoms and molecules. All matter can exist in three states: solid, liquid and gas.

Solids: keep their shape and volume. The particles of the substance vibrate in place. The vibration isn't strong enough to overcome the attraction of the particles and cause them to separate. As a result, the forces between the particles cause them to lock together.

Liquids don't have a shape of their own. They take on the shape of the container they are in. Liquids do have a definite volume, though. The particles of a liquid move faster than particles of a solid. As a result, the particles in a liquid can overcome some of the attraction between them. Unlike the particles in a solid, which are locked together, the particles in a liquid can flow around and over each other.

Gases can flow throughout a room. Particles in a gas move so fast they are able to overcome the attraction between them. The particles of a gas will drift apart and will spread out in all directions. They do this whether they are filling up a balloon, a room, or all the Earth's atmosphere.



Changing the state of matter of a substance is a physical change. It is usually caused by changing the temperature or surrounding pressure of a substance.

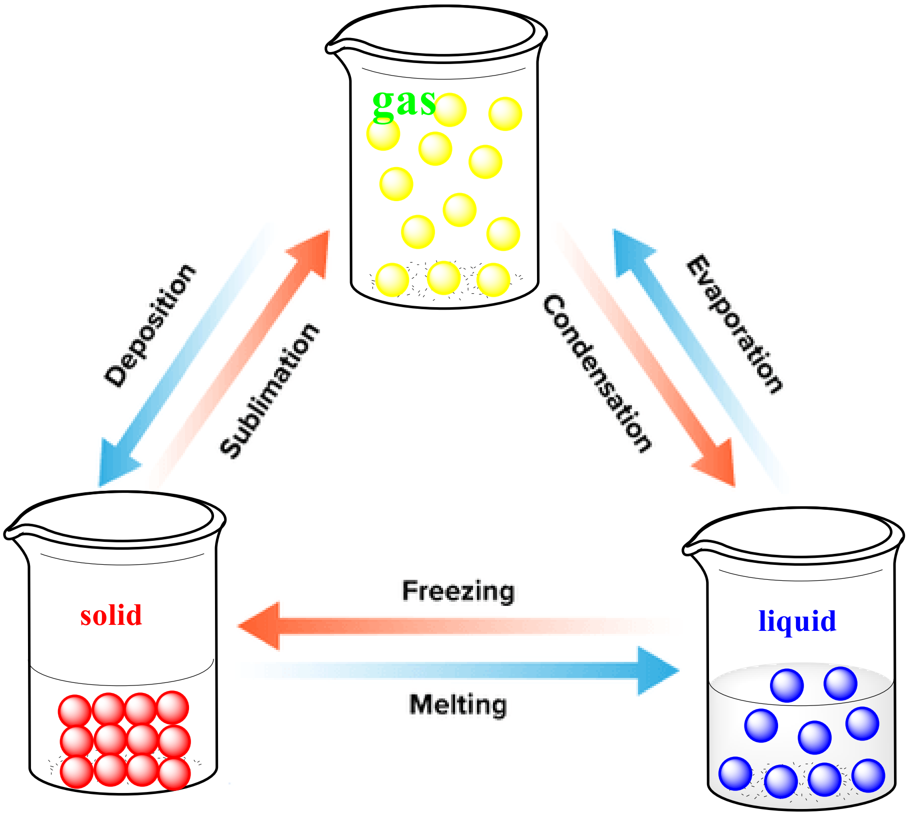
Solid, liquid and gas **expand when heated**. They **contract when cooled**. The increase in volume of matter due to an increase in temperature is called **thermal expansion**.

When heat is added to a solid, its temperature will rise to a certain point where the solid starts to melt. This point is called the **melting point**. When heat is removed from the liquid, its temperature drops to a certain point where the liquid starts to freeze. This point is called the **freezing point**.

The temperature at which a liquid changes into a gas is called the **boiling point**.

The change of state from a liquid to a gas is called **evaporation**. The change of state from a gas to a liquid is called **condensation**.

If solids have enough vapor pressure at a particular temperature then they can change directly into air. The direct change of state from solid to gas is called **sublimation**.



III- Atoms, elements and compounds

Atoms:The basic building block of all matter is called an atom.

Atoms are a collection of various subatomic particles containing negatively charged electrons, positively charged protons and neutral particles called neutrons. Each atom has its own unique number of protons, neutrons and electrons.

Examples: $^{16}_{8}O$, $^{26}_{56}Fe$, $^{11}_{23}Na$.

The Elements: is a substance that cannot be decomposed into simpler substances by chemical changes.

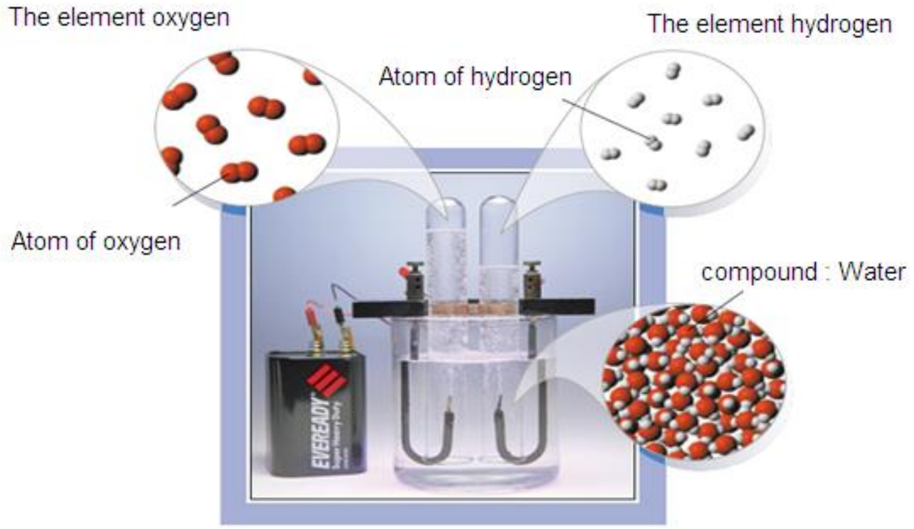
- At present, **118 elements** have been positively identified.

Table 1.3. Some Common Elements and Their Symbols

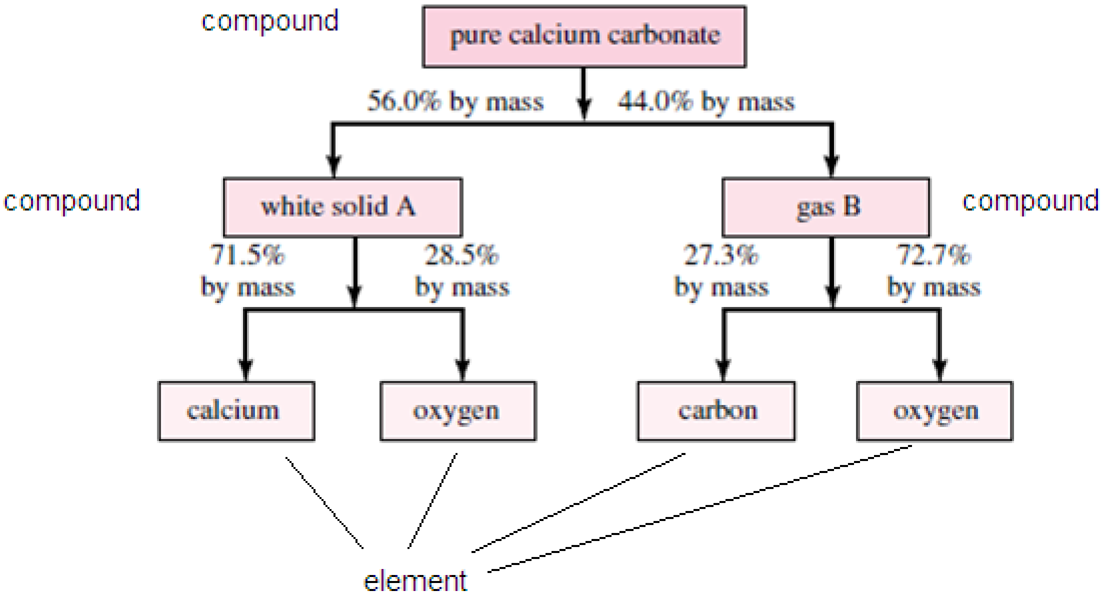
Name	Symbol	Name	Symbol	Name	Symbol
Aluminum	Al	Fluorine	F	Oxygen	O
Arsenic	As	Phosphorus	P	Barium	Ba
Hydrogen	H	Platinum	Pt	Bromine	Br
Iodine	I	Potassium	K	Calcium	Ca
Iron	Fe	Silicon	Si	Carbon	C
Lead	Pb	Silver	Ag	Chlorine	Cl
Magnesium	Mg	Sodium	Na	Chromium	Cr
Mercury	Hg	Sulfur	S	Cobalt	Co
Nickel	Ni	Tin	Sn	Copper	Cu
Nitrogen	N	Zinc	Zn	Gold	Au

Samples of mercury, silver, and sulfur

A compound: is a substance that can be decomposed by chemical means into simplersubstances, always in the same ratio by mass.



Example:



- ➢ All the many kinds of matter can be classified as either pure substances or mixtures. Pure substances, in turn, can be either elements or chemical compounds.

Chemical Compounds: A chemical compound is a pure substance that is formed when atoms of two or more different elements combine and create a new material with properties completely unlike those of its constituent elements.

For example, when atoms of sodium (a soft, silvery metal) combine with atoms of chlorine (a toxic, yellow-green gas), the familiar white solid called sodium chloride $NaCl$(table salt) is formed.

Mixtures:A mixture is a combination of two or more substances in which the substances retain their distinct identities.

Some examples: air, soft drinks, milk, and cement.

- Mixtures can be further classified as either **heterogeneous** or **homogeneous**.

Heterogeneous mixtures are those in which the mixing is not uniform and which therefore have regions of different composition.

Examples: Sand with sugar, water with gasoline, and dust with air.

Homogeneous mixtures are those in which the mixing is uniform and which therefore have a constant composition throughout.

Examples: Air is a gaseous mixture of (primarily) oxygen and nitrogen, seawater is a liquid mixture of (primarily) sodium chloride dissolved in water, and brass is a solid mixture of copper and zinc.

With liquids it’s often possible to distinguish between a homogeneous mixture and a heterogeneous one simply by looking. Heterogeneous mixtures tend to be cloudy and will separate on standing, whereas homogeneous mixtures are often transparent.

IV- Mole and Avogadro number

The concept of a mole as applied to atoms is especially useful. It provides a convenient basis for comparing the masses of equal numbers of atoms of different elements.

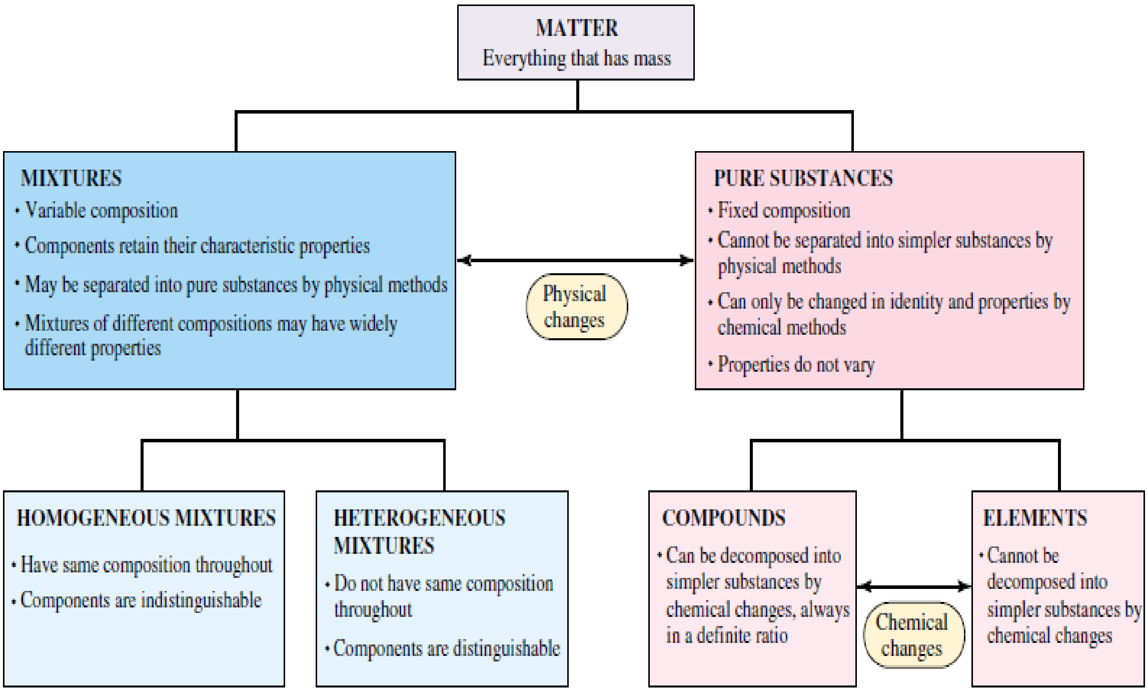
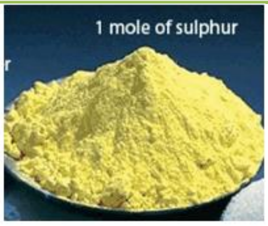
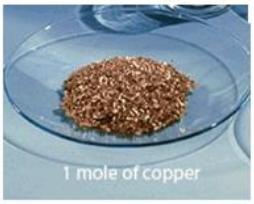
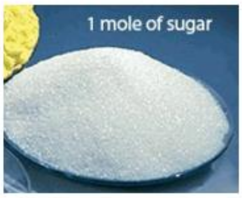


Table 1.4. Mass of one mole of atoms of some common elements.

Element	A sample with a mass of	Contains
Carbon	12 g of C	6.02×10^{23} C atoms or 1 mol of C atoms
sulfur	32.1 g S_8	6.02×10^{23}S atoms or 1 mol of S atoms
Gold	197 g of Au	6.02×10^{23}Au atoms or 1 mol of Au atoms
Hydrogen	1 g of H_2	6.02×10^{23}H atoms or 1 mol of H atoms







The number of atoms in a 12g sample of carbon12 is called Avogadro's number (to which we give the symbol N). Recent measurements of this number give the value **6.0221367×10^{23}**.

Exercise 2:

How many molecules are there in 20.0 g of benzene, C6H6?

I- Atomic mass unit

The mass of a single atom in grams is much too small a number for convenience, and chemists therefore use a unit called an atomic mass unit (amu), also known as a dalton (Da). One amu is defined as exactly one twelfth the mass of an atom of ${}^{12}_{6}C$and is equal to the value of :

$$\mathbf{1.660\,539 \times 10^{-24}\ g = 1.660539 \times 10^{-27}\ kg.}$$

$$\begin{cases} \text{One mole of carbon} \rightarrow \ N \text{ atoms of carbon} \ \rightarrow \ 12\text{ g} \\ \text{One atom of carbon} \ \rightarrow \ \text{mass of one atom of carbon} \end{cases} \Rightarrow \text{mass of one atom of carbon} = \frac{12}{N}$$

$$1\text{ amu} = \frac{1}{12} \times \frac{12}{N} = \frac{1}{N} \Rightarrow \mathbf{1amu = 1.66 \times 10^{-24}\ g}$$

Exercise 3.

- How many moles of Zinc are there in a sample of 23.3 g of Zn?
- How many atoms of Zn are there in this sample?
- What is the mass (in grams and in amu) of 4.52×10^{23} Zn atom?

II- Atomic and molecular molar mass, molar volume

1- Atomic molar mass

An element's atomic mass is the weighted average of the isotopic masses of the element's naturally occurring isotopes.

Example:Carbonoccurs on Earth as a mixture of two isotopes, ${}_{6}^{12}C$ (12amu,98.89% natural abundance) and ${}_{6}^{13}C$ (13.0034 amu, 1.11% natural abundance) (A third carbon isotope, ${}_{6}^{14}C$, its abundance is so low that it can be ignored when calculating atomic mass). The average isotopic mass—that is, the atomic mass—of a large collection of carbon atoms is 12.011 amu.

2- Molecular molar mass

Ethanol, whose molecular formula is $C2H5OH$, has a molecular mass of 46.1 amu and a molar mass of 46.1 g/mol.

The molecular molar mass of a substance is the mass of one mole of the substance. Carbon-12 has a molar mass of exactly 12 g/mol, by definition. For all substances, the molar mass in grams per mole is numerically equal to the formula mass in atomic mass units.

Exercise 4:

What is the mass in grams of a chlorine atom, Cl? What is the mass in grams of a hydrogen chloride molecule, HCl?

3- Molar volume

In 1811, Amedeo Avogadro postulated thatat the same temperature and pressure, equal volumes of all gases contain the same number of molecules. This Law can also be stated as follows:At constant temperature and pressure, the volume, V, occupied by a gas sample is directly proportional to the number of moles, n, of gas.

$$V = k\,n \quad \text{or} \quad \frac{V}{n} = k \text{ (constant P, T)}$$

For two samples of gas at the same temperature and pressure, the relation between volumes and numbers of moles can be represented as:

$$\frac{V_1}{n_2} = \frac{V_2}{n_2} \text{(constant P, T)}$$

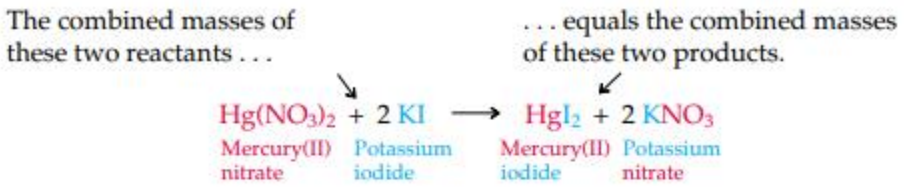
The standard molar volume of an ideal gas is taken to be **22.414 liters per mole** at constant P, T.

I- Weight law:, Conservation of mass, chemical reaction, Qualitative aspect of matter, Quantitative aspect of matter

1- Conservation of mass Law (Lavoisier)

Lavoisier demonstrated by careful measurements that when combustion is carried out in a closed container, the mass of the combustion products exactly equals the mass of the starting reactants.

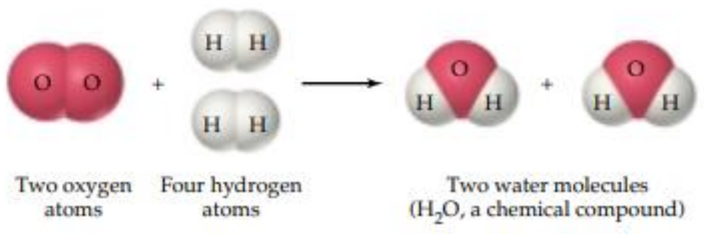
LAW OF MASS CONSERVATION Mass is neither created nor destroyed in chemical reactions. That means: the total mass remains constant during a chemical change.



2- A chemical reaction

A chemical equation is written in a standard format, in which the starting substances, or **reactants**, are on the left, the final substances, or **products**, are on the right, and **an arrow** is placed between them to indicate **a transformation**. The numbers and kinds of atoms are the same on both sides of the reaction arrow, as required by the law of mass conservation.

$$O_2 + 2\,H_2 \longrightarrow 2\,H_2O$$



A chemical equation also indicates the relative amounts of each reactant and product in a given chemical reaction. Then the equationcanbewritten :

$$CH_4 \quad + \quad 2O_2 \quad \rightarrow \quad CO_2 \quad + \quad 2H_2O$$

1 mol 2mol 1mol 2mol

This interpretation tells us that one mole of methane reacts with two moles of oxygen to produce one mole of carbon dioxide and two moles of water.

A balanced chemical equation may be interpreted in terms of moles of reactants and products and **Never start a calculation involving a chemical reaction without first checking that the equation is balanced.**

Exercise 5:

1- How many moles of water could be produced by the reaction of 3.5 mol of methane with excess oxygen (i.e., more than a sufficient amount of oxygen is present).

Chemical equations describe **reaction ratios**, that is, the mole ratios of reactions and products as well as the relative masses of reactants and products.

We use the coefficients to get the mol ratio of any two substances we want to relate then we apply it as:

Moles of desired = (moles of substance given)× (mole ratio from balanced chemical equation)

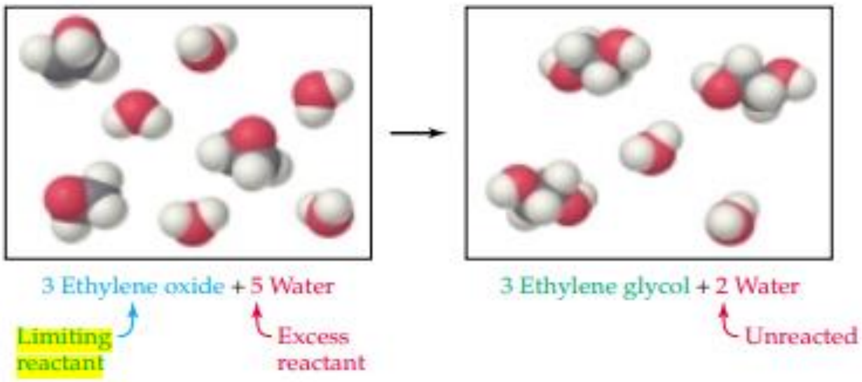
Mole substance must appear in the numerator of the mole ratio, i.e., do not just write $\frac{\text{mol}}{\text{mol}}$, write $\frac{\text{mol of something}}{\text{mol of something else}}$ and giving the formulas of the two substances involved.

Exercise 6:

What mass of oxygen is required to react completely with 1.2 mol of CH_4?

- **The Limiting Reactant Concept**

The substance that was used up first, called the **limiting reactant**, the other reactant is said to be the **excess reactant**. The limiting reactant is not necessarily the reactant present in the smallest amount.



Exercise 7:

What mass of CO_2 could be formed by the reaction of 16 g of CH_4 with 48 g of O_2?

Percent Yields from Chemical Reactions

The theoretical yield from a chemical reaction is the yield calculated by assuming that the reaction goes to completion.

$$\text{Percent yield (\%)} = \frac{\text{actualyieldofproduct}}{\text{theoreticalyieldofproduct}} \times 100$$

Exercise 8:

A 15.6 g sample of C_6H_6 is mixed with excess HNO_3. We isolate 18 g of $C_6H_5NO_2$. What is the percent yield of $C_6H_5NO_2$ in this reaction

3- Qualitative aspect of matter

Qualitative Property: is a characteristic of a substance that can be described but not measured. You can describe matter using the following terms.

- **To describe all substances**:
  - ✓ clarity : transparent (clear), translucent (cloudy), opaque
  - ✓ colour:colourless, red, orange, blue, white, etc
  - ✓ odour:odourless, sweet, sour, burnt, aromatic, fragrant, nauseating, sharp, acrid, choking
- **To describe solids only**:
  - ✓ texture : crystalline, granular, waxy, flaky
  - ✓ lustre: shiny, dull, metallic, greasy, glassy
  - ✓ hardness : hard, soft, flexible, brittle
- **To describe liquids** only: viscosity

4- Quantitative aspect of matter

Quantitative Property: is a characteristic of a substance that can be measured numerically.

Stoichiometry: Description of the quantitative relationships among elements and compounds as they undergo chemical changes.Itis the calculation of the quantities of reactants and products involved in a chemical reaction

Reaction stoichiometry: Description of the quantitative relationships among substances as they participate in chemical reactions.

- Such calculations are fundamental to most quantitative work in chemistry

Density : is the mass of an object divided by its volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \Rightarrow d = \frac{m}{V}$$

Where d, m, and V denote density, mass, and volume, respectively

The SI-derived unit for density is the **kilogram per cubic meter (kg/m^3)**. Therefore, **grams per cubic centimeter (g/cm^3)**and its equivalent, **grams per milliliter (g/mL)**, are more commonly used for solid and liquid densities.

Percentage Composition: A chemical formula may be used to compute the percentage composition of a compound; that is, the percentage by weight of each type of atom in the compound.

Solution concentration is sometimes expressed in terms of the mass percentage of solute—that is, the percentage by mass of solute contained in a solution.

$$\text{Mass percentage of solute (\%)} = \frac{\text{massofsolute}}{\text{massofsolution}} \times 100$$

Molarity: A solution that contains one mole of solute per liter of solution is known as a one molar solution; it is abbreviated 1.00 M. In general

$$\text{molarity of solution} = M = \frac{\text{molesofsolute}}{\text{literofsolution}}$$

Molality: The molality of a solution is the moles of solute per kilogram of solvent.

$$\text{molality of solution} = N = \frac{\text{molesofsolute}}{\text{kilogramsofsolution}}$$

Problem:

- A piece of gold ingot with a mass of 0.301 kg has a volume of 15.6 cm^3. Calculate the density of gold.

- Calculate the percentages of oxygen and hydrogen in water, H_2O.
- How would you prepare 425 g of an aqueous solution containing 2.40% by mass of sodium acetate, $NaC_2H_3O_2$?
- A compound contains 90.6% Pb and 9.4% O by weight. Find the empirical formula.
- What volume of 0.250 M Na_2CrO_4 will be needed in order to obtain 8.10 g of Na_2CrO_4?
- What is the molality of a solution containing 5.67 g of glucose dissolved in 25.2 g of water?
- A solution is prepared by dissolving 0.131 g of a substance in 25.4 g of water. The molality of the solution is 0.056 m. What is the molecular mass of the substance?

CHAPTER 2

MAIN CONSTITUENTS OF MATTER

Chapter contents

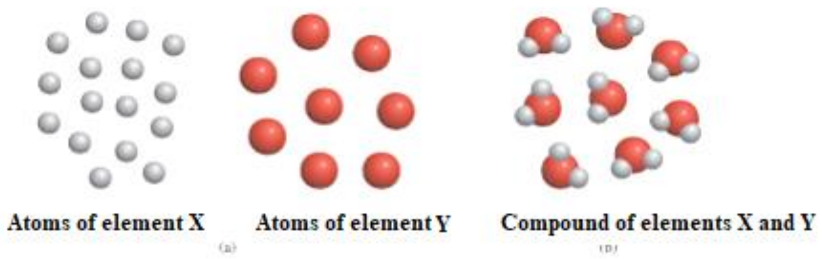
- **Introduction: Faraday's experiment: relationship between matter and electricity,**
- **Highlighting the constituents of matter and atom, some physical properties (mass and charge),**
- **Rutherford planetary model,**
- **Presentation and characteristics of the atom (Symbol, atomic number Z, mass number A, number of protons, neutrons and electrons),**
- **Isotopia and relative abundance of different isotopes,**
- **Separation of isotopes and determination of the atomic mass and the average mass of an atom: Mass spectrometry: Bainbridge spectrograph,**
- **Energy of connection and cohesion of the nuclei,**
- **Stability of atomic nuclei**

CHAPTER 2

MAIN CONSTITUENTS OF MATTER

I- Introduction

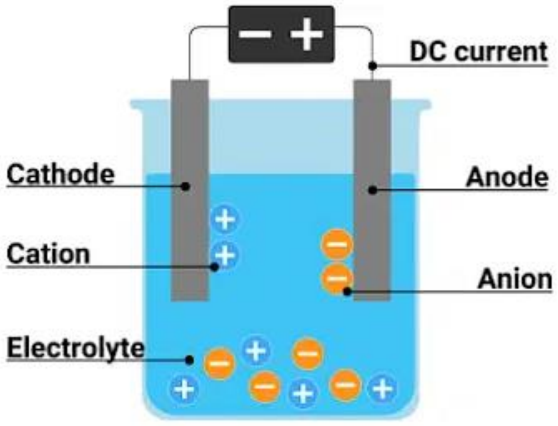
The modern version of atomic theory was laid out by John Daltonin 1803, who postulated that elements are composed of extremely small particles, called atoms, and that all atoms of a given element are identical, but they are different from atoms of all other elements.



II- Faraday's experiment: relationship between matter and electricity

Some of the earliest evidence about atomic structure was supplied in the early 1800s by the English chemist **Humphry Davy** (**1778–1829**). He found that when he passed electric current through some substances, the substances decomposed. He therefore suggested that the elements of a chemical compound are held together by electrical forces.

In **1832– 1833**, **Michael Faraday**, Davy’s student, discovered that the amount of substance produced at an electrode by electrolysis depends on the quantity of charge passed through the cell.



To find out how many moles of electrons pass through a cell in a particular experiment, we need to measure the electric current and the time that the current flows.

The number of coulombs of charge passed through the cell equals the product of the current in amperes (coulombs per second) and the time in seconds:

$$\text{Charge (C)} = \text{Current (A)} \times \text{Time (s)} \Rightarrow \mathbf{q = A\,.t}$$

The electric charge on 1 mol of electrons is 96,485 C/mol e^-,so the number of moles of electrons passed through the cell is:

$$\text{Moles of e- = Charge (C)} \times \frac{1\text{ mol e}^-}{96{,}500\text{ C}}$$

Studies of Faraday's work by **George Stoney** (1826–1911) led him to suggest in **1874** that units of electric charge are associated with atoms. In 1891, he suggested that they be named **electrons**.

Table 1. Derived units (where E and B are the electric and magnetic fields, L is the length, t is the time, q is the charge, x is the distance, U is the potential)

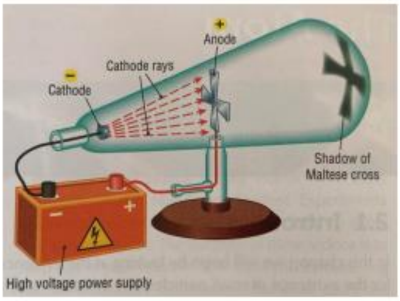
Quantity	Definition of quantity	SI Unit	Equation
Area	Lengthsquared	m^2	$A= L\,.L$
Volume	Length cubed	m^3	$V= A\,.\,L$
Density	Mass per unit volume	kg/m^3	$d = m/V$
Speed	Distance traveled per unit time	m/s	$\nu = x/t$
Acceleration	Speed changed per unit time	m/s^2	$\gamma = \nu/t$
Magneticfield	force per (speed times charge)	N.s/m.C = kg/s.C = Tesla	$B = F.t/x.q$
Electric field	volt per metre	(V/m)	$E = U/d$
Force **Electric force** **Magnetic force**	- Mass times acceleration of object - Charge times electric field - charge times speed times magnetic field	$kg.m/s^2$(= newton, N) (Coulomb × Volt)/m C.(m/s).T	$F = m\,.\gamma$ $Fe = q\,E$ $F_m = q.\nu.\,B$
Pressure	Force per unit area	$kg/(m.s^2)$ (=pascal,Pa)	$P = F/A$
Energy	Force times distance traveled Charge times volt	$kg.m^2/s^2$(=joule, J) C. Volt	$E = F.\,x$ $E = q.U$

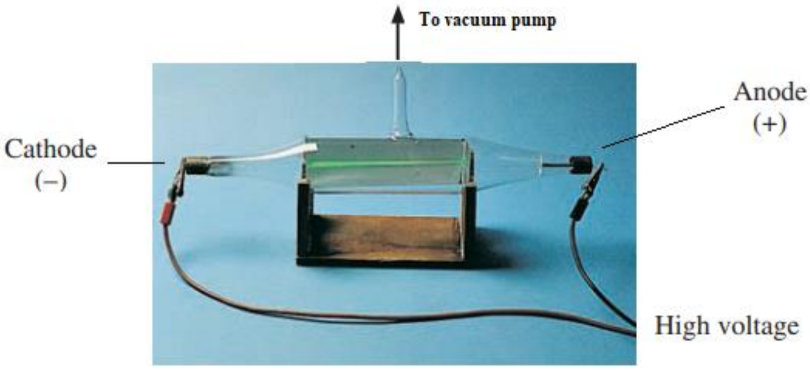
III- Highlighting the constituents of matter and atom

1- Discovery of SubatomicParticles

➢ Discovery of the Electron

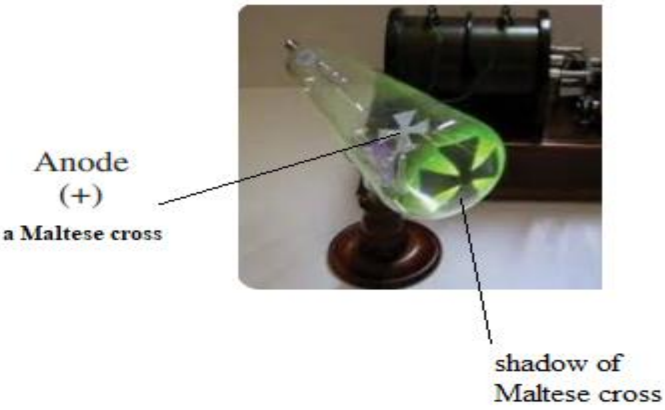
In 1875 **William Crookes** (English chemist)used a vacuum tubecalled**cathode ray tube**;along glass tube with an electrode at each end, inside the tube there was gas at low pressure(**0.01 mmHg)** andathigh-voltage (**50000 v**).



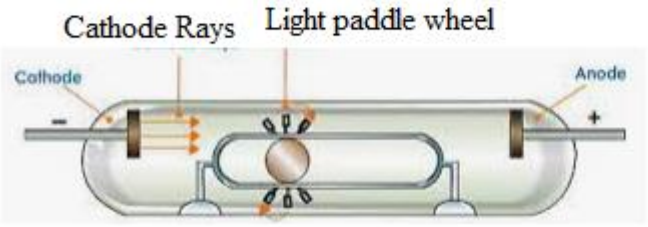


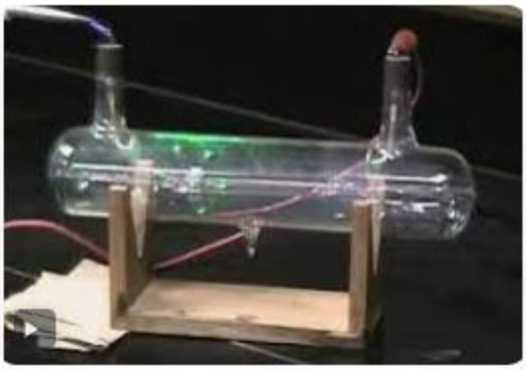
When the high-voltage current is turned on, the glass tube emits a greenish light. Experiments showed that this greenish light is caused by the interaction of the glass with cathode rays, which are rays that originate from the cathode(negative electrode).

- These Rays travelled from **cathode** (negative electrode)to**anode**(positive electrode)they are called **cathode rays.**
- They travelled in straight lines – to show the presence of radiation he placed a Maltese cross inside the tube – a sharp shadow in glow formed at end of tube.

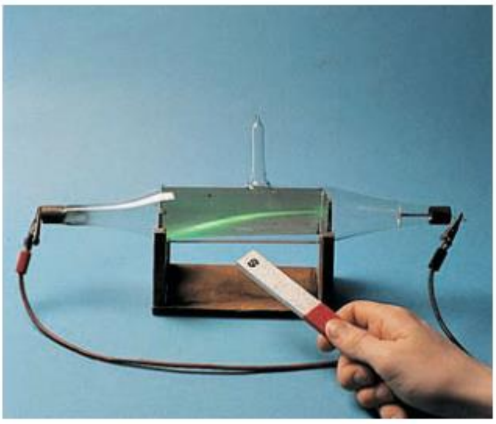


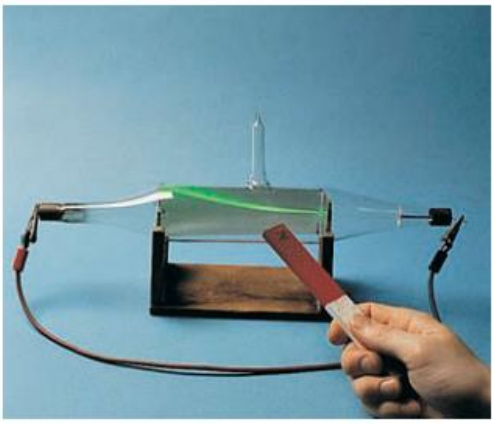
Crookes carried out a second experiment to investigate the properties of cathode rays. It consisted of a light paddle wheel mounted on rails in front of the cathode.

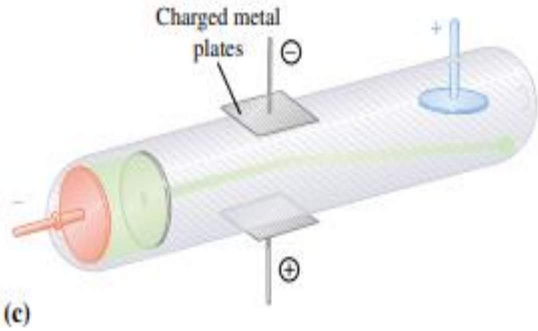




- When current on – paddle wheel rotated and travelled down the tube.Vanes always turned away from the cathode**: they were struck by particles from the cathode.**
- The beam of the ray bends away from the negatively charged plate and toward the positively charged platein an electric field.Interaction of cathode rays with a magnetic field is also consistent with negative charge







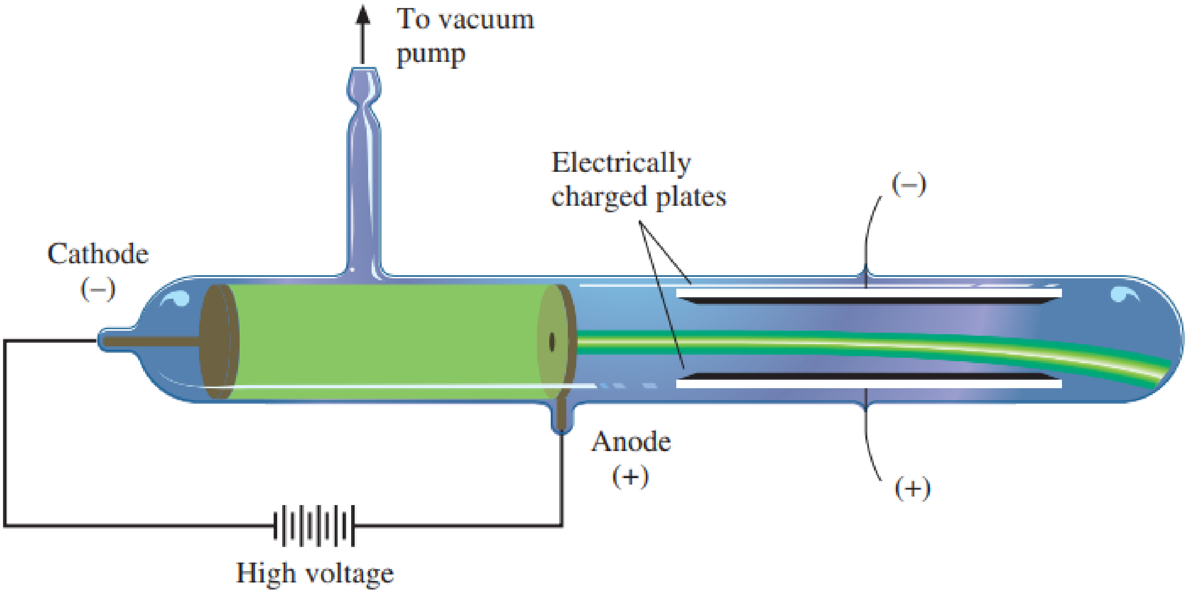
Crookes deducted properties of the cathode:

- **Cathode rays travel in straight lines (**an object placed in a beam of ray casts a shadow)**.**
- **Cathode rays cause glass to fluorescence when they stroke it.**
- **Cathode rays possess enough energy to move a paddle wheel that means,Cathode rays(electrons) have mass.**
- **The cathode ray (electrons) consists of a beam of negatively charged particles** (as demonstrated by their deflection in an electric field)**and they are constituents of all matter.**

➢ Physical properties of electron

a. Joseph John Thomson (calculation of e/m_e ratio) (Nobel 1906)

In **1897**, an English physicist, J. J. Thomson, used a cathode ray tube and his knowledge of electromagnetic theory to determine the ratio of electric charge to the mass of an individual electron**e/m_e**.



When in an electric field, charged particles experience a force which can accelerate them to high velocities. If q is the charge of the particle and E is the magnitude of the electric field, then force F is given as:

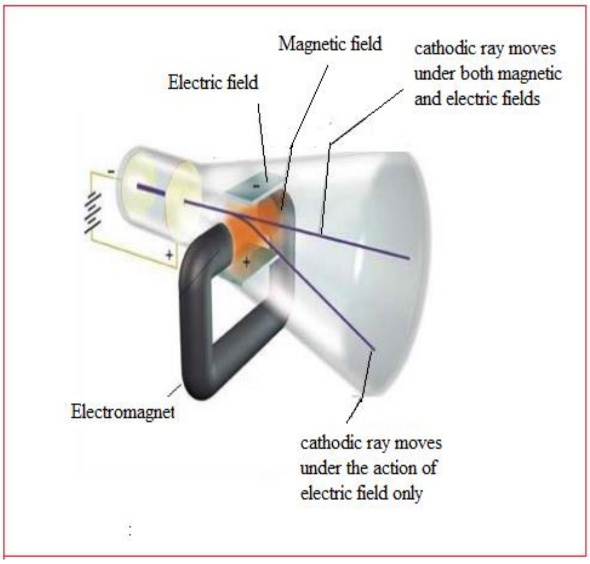
$$F_e = q \cdot E$$

A potential difference U exists across the two ends of the field, and the work (W) done on the particle when accelerated across the field would be:

$$W=q\,.\,U$$

A charged particle of charge q moving with a velocity v in a magnetic field of strength B also experiences a force. This force, F_m is given by:

$$F_m=q\,(v \times B)$$



- It is important to understand that the magnetic field can never change the magnitude of the velocity of a substance. It can only change the direction.

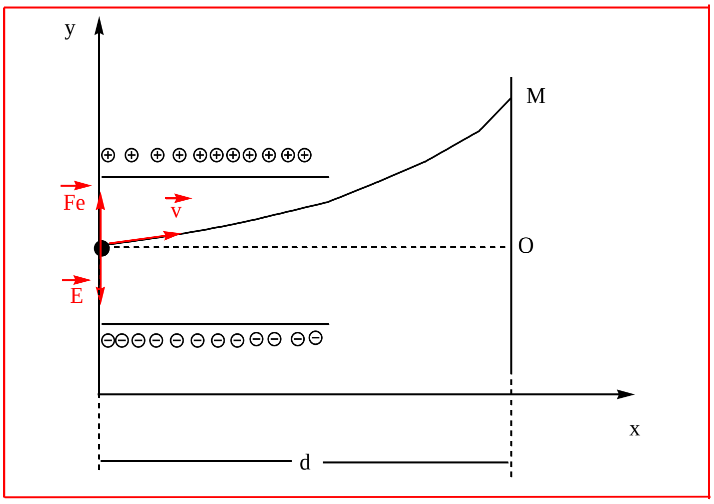
Electric (E) and magnetic fields (B) are adjusted such that the beam of electrons is not deflected and travel in straight lines. This means that the sum of all the forces acting on it is equal to zero.

$$\|\overrightarrow{Fe}\| + \|\overrightarrow{Fm}\|=0 \quad \Rightarrow q.B.v = q.E \Rightarrow \quad \boxed{v = \frac{E}{B}}$$

By turning off the magnetic field, Thomson could measure the deflection of the cathode rays in the electric field alone.In this case, Electrons (mass m_e) gain acceleration (γ), which can be calculated as follows:

$$\sum F_{ex} = m_e.\gamma = F_e \qquad \Rightarrow q.E = m_e\gamma \Rightarrow \qquad \boxed{\gamma = \frac{q.E}{m_e}}$$

Suppose that an electron with charge"-e" and mass m is moving to the right, as shown in Figure at the right. It passes through a region of length d in which there is an electric field E pointing up. If the electron is deflected upward by a distance OM as it passes through the field.



- The velocity $v_x$of the particles perpendicular to the field remains constant (abscise axis).

$$v_x = x/t \quad \Rightarrow \quad t = x/v_x$$

- The velocity v_y of the particles parallel to the field remains accelerate (ordinate axis).

$$y = oM = \frac{1}{2}\gamma.t^2 \Rightarrow \qquad y = \frac{1}{2}.\frac{q.E}{m_e}.\frac{X^2}{V^2}$$

noted that: q = e (electron charge) ; x = d (distance travelled on abscise axis) ; y=OM (distance travelled on ordinate axis)

The charge to mass ratio of the electron is given by:

$$\boxed{\frac{e}{m_e} = \frac{2.OM.v^2}{E.d^2}}$$

The unknown quantity e/m is expressed in terms of the known quantities d, E, v, and l. Notice that the deflection of the electron in this example and in Thomson's tube determines neither the value of enor the value of m, but only their ratio.

$$\boxed{e/m_e = 1.7589 \times 10^{11} \text{ coulomb/kg}}$$

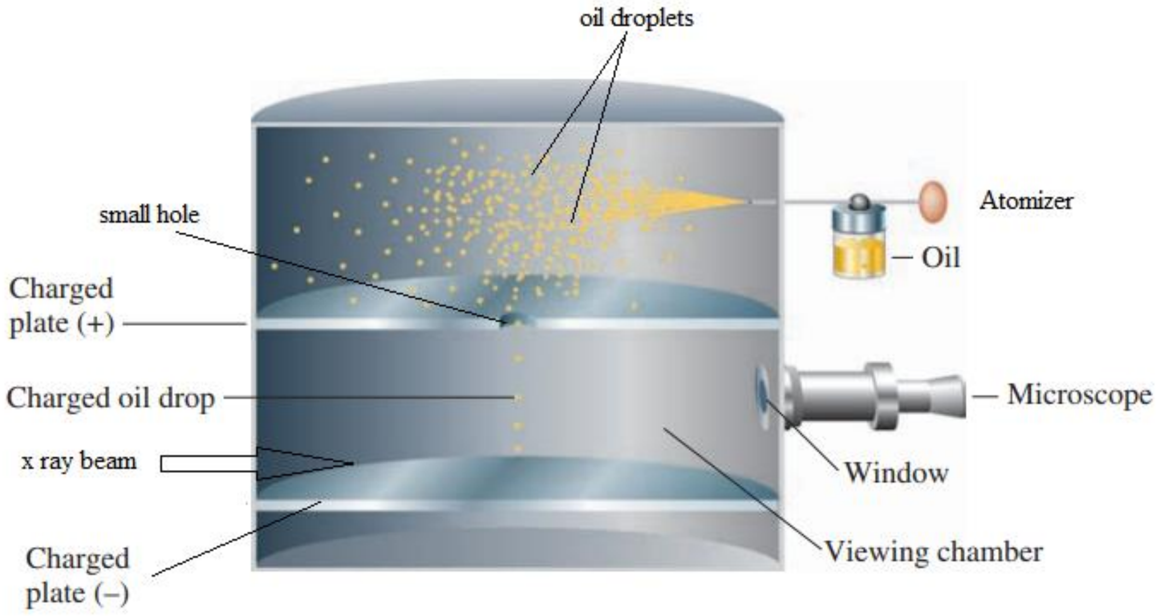
Exercise 1.

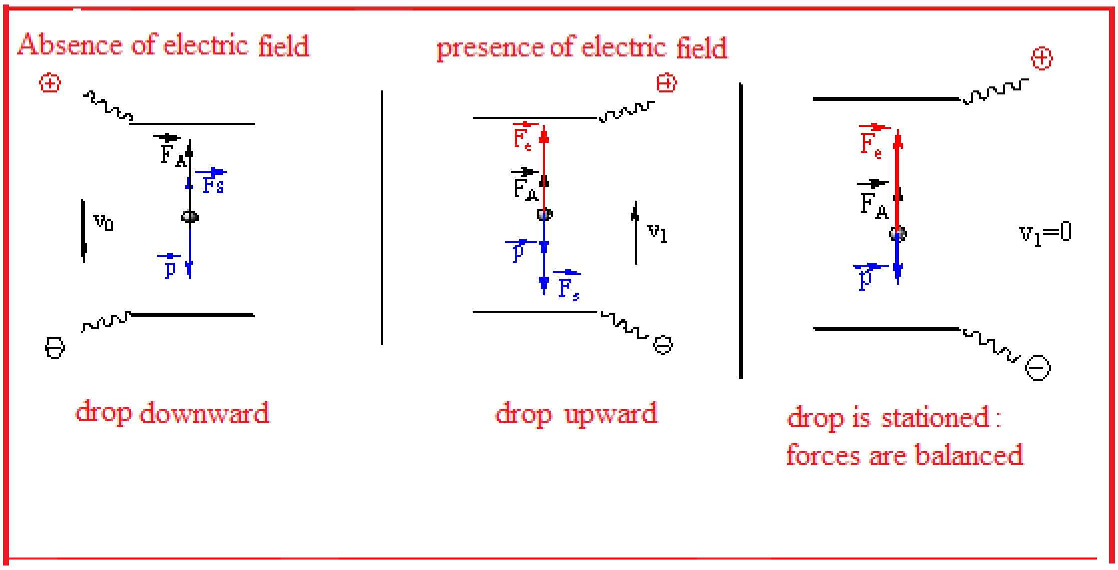
A beam of electrons having a velocity of 2.00 × 10^7 m/s enters a 2 × 10^4 volt/m electric field situated between two plates separated of a distance d = 10 cm. This beam of electrons is deflected once the magnetic field is removed by an amount of 4.4 cm.Determine e/me from these observations, and compare the result with the known value. (1.76 × 10^{11} C/kg).

b. Millikan’s oil-drop experiment

In **1909** the U.S. physicist **Robert Millikan** performed a series of ingenious experiments in which he obtained the charge on the electron by observing how a charged drop of oil falls in the presence and in the absence of an electric field.

Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field ($E = V / d$) lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops.





❖ When the oil drop is stationed within the volume, once a voltage is applied across the plates, there is an electric force, *F* , acting upwards. This is given by:

$F_e = E . q$ where **q** is the charge on the oil drop and **E** is the field strength.

The electric field can be expressed as a function of the voltage U across the plates and the spacing d between them:

$E = U/d$ where **U** is the voltage on the plates and **d** is their separation.

The downward force acting on the oil drop is due to the gravitational pull on the drop:

The drop is being pulled down by its weight **$p = m.g$**(the gravitational pull)

Where $m = \rho.V = \rho.\frac{4}{3}\pi r^3 \Rightarrow p = (4/3)\pi r^3.\rho.g$

Where ρ in **kg/m^3**is the density of the oil and **g** = Acceleration of gravity in **m/s^2**.

Assuming that the oil drop is approximately spherical, its volume is given by the following formula:

$$V = (4/3)\pi r^3$$

Where r is the radius of the oil drop.

There is a third force acting on the oil drops. The buoyancy due to the surrounding air between the plates introduces an upward thrust: the plate introduces an upward thrust:

$F_A = g' m \qquad \Rightarrow F_A = (4/3)\pi r^3.\rho_o.g$

Where ρ_0 is the density of the air (1.2929 kg/m^3).

In the correct conditions, the electrostatic force and the force of gravity can be balanced, such that the oil drop is brought to rest. In this case, we can express the charge on the oil drop as follows:

$$F_e = P \qquad \Rightarrow \mathbf{q = \frac{mgU}{d}}$$

Therefore the equation for the charge of the oil drop can be reexpressed as:

$$\mathbf{q = \frac{d}{U}\cdot\frac{4}{3}\pi r^3 (\rho_{oil} - \rho_{air})}$$

❖ When switching off the voltage and letting the drop fall. As the drop falls down through the viscous air, it experiences an upward drag force given by Stokes's law as follows:

When the oil drop is in the electric field, there is an electric force, F ,the gravitational pullP, the buoyancy force and Stokes's force acting upwards. This is given by:

$$F_{s\uparrow} = 6\pi\eta r v_o$$

In this equation, $\eta$is the viscosity of air (1.81 × 10^{-5} kg/m.s) and$v$is the speed of the oil drop.

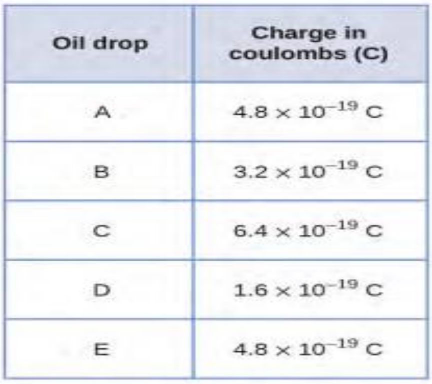
Using this expression and applying Newton's 2nd Law to a falling oil drop under the influence of the viscous and buoyant force, one can show that the radius of the oil drop is:

$$\boxed{\mathbf{r = 3\sqrt{\frac{\eta v_0}{2(\rho - \rho_0)g}}}}$$

And the charge on the droplet is given by:

$$\boxed{\mathbf{q = \frac{6\pi\eta r}{E}(v_1 + v_0)}}$$

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6 × 10^{-19} C.



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Millikan concluded that this value must therefore be a fundamental charge, the charge of a single electron, with his measured charges due to an excess of one electron (1 times 1.6 × 10^{-19} C), two electrons (2 times 1.6 × 10^{-19} C), three electrons (3 times 1.6 × 10^{-19} C), and so on, on a given oil droplet.

Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio wasalready known due to Thomson's research (1.759 × 10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

Because $\frac{e}{m} = 1.758\,820 \times 10^{8}\ \mathrm{C/g}$

then $m = \frac{e}{1.758\,820 \times 10^{8}\ \mathrm{C/g}} = \frac{1.602\,176 \times 10^{-19}\ \cancel{\mathrm{C}}}{1.758\,820 \times 10^{8}\ \frac{\cancel{\mathrm{C}}}{\mathrm{g}}}$

$= 9.109\,382 \times 10^{-28}\ \mathrm{g}$

$$\boxed{e = 1.6 \times 10^{-19}\text{coulomb}}$$

$$\boxed{m_e = 9{,}108 \times 10^{-31}\text{Kg}}$$

Exercise 2

An oil drop has a mass of 8.22×10^{-11} kg and is balanced in an electric field of 4.36×10^{7} N/C.

a) Calculate the charge on the oil drop. ($q = +1.85 \times 10^{-17}$ C).

b) How many electrons would need to have been lost or gained? (≈ 116 e^{-}lost) ?

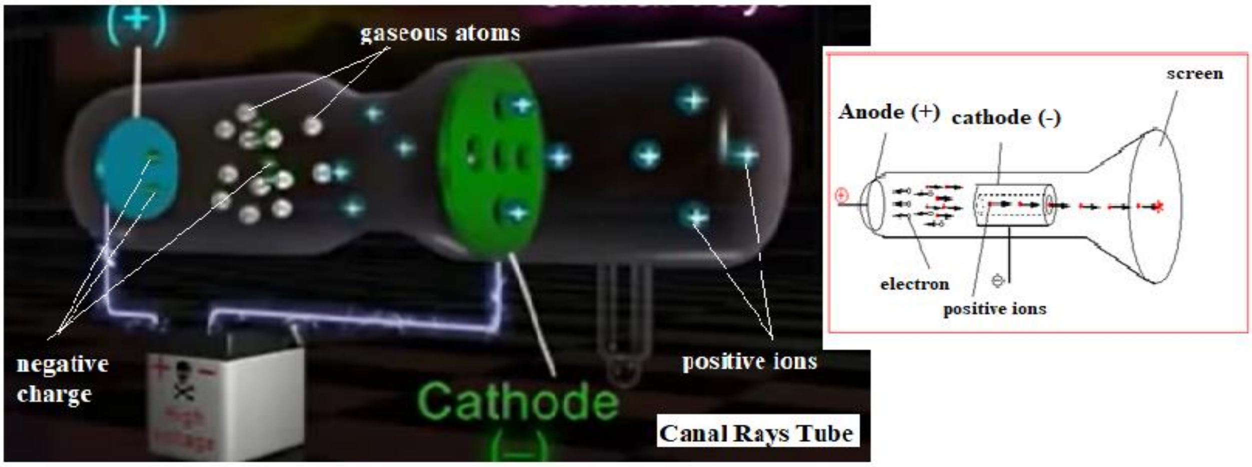
c) Supposed that the oil drop is now experiencing a downward acceleration of 6.1 m/s^2. Calculate the electric force. (3.05×10^{-10} N).

d) Supposed that the oil drop is now experiencing a upward acceleration of 17.4 m/s^2 . Calculate the electric force. (6.2×10^{-10} N).

➢ Discovery of the proton

In **1886**, **Eugen Goldstein** (1850–1930) first observed that a cathode-ray tube also generatesa stream of positively charged particles that moves toward the cathode. This faint luminous ray was seen extending from the holes in the back of the cathode.

These were called **canal rays** because they were observed occasionally to pass through a channel, or“canal,” drilled in the negative electrode.



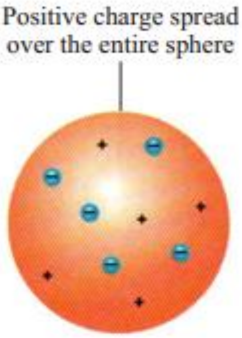
https://www.youtube.com/watch?v=1JX7iTm3Uw8

These *positive rays*, or *positive ions*,are created when the gaseous atoms in the tube lose electrons. Positive ions are formedby the process

Gas atom → cation^{+} + e^{-}

Different elements give positive ions with different *e/m* ratios. The regularity of the *e/m*values for different ions led to the idea that there is a unit of positive charge and that itresides in the **proton.** The proton is a fundamental particle with a charge equal in magnitudebut opposite in sign to the charge on the electron. Its mass is almost 1836 times thatof the electron.

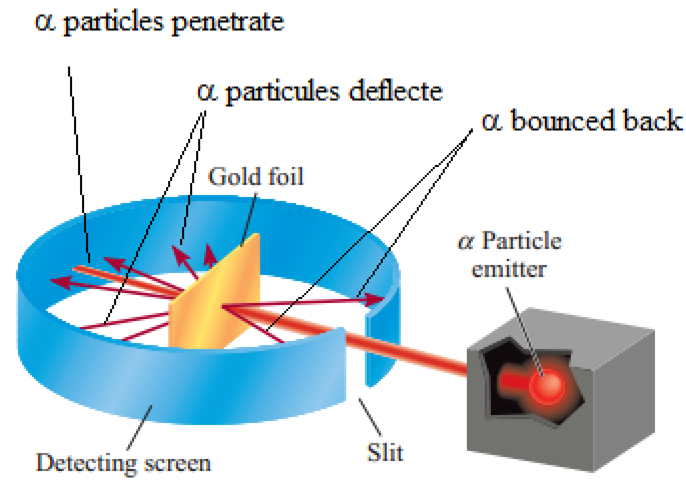
By the early 1900s, two features of atoms had become clear: They contain electrons, and they are electrically neutral. To maintain electrical neutrality, an atom must contain an equal number of positive and negative charges. On the basis of this information, Thomson proposed that an atom could be thought of as a uniform, positive sphereof matter in which electrons are embedded. Thomson’s so-called “plumpudding” model was the accepted theory for a number of years.



IV- Rutherford planetary model

In **1910** the New Zealand physicist **Ernest Rutherford** and his collaborators, decided to useαparticles (positive particlesprovided from radioactive polonium)to probe the structure of atoms. They carried out a series of experiments using very thin foils of gold and other metals as targets for particles from a radioactive source.

- They observed that the majority of particles penetrated the foil either undeflected or with only a slight deflection.
- They also noticed that every now and then anαparticle was scattered (or deflected) at a large angle.
- In some instances, an *α*particle actually bounced back in the direction from which it had come!
- This was a most surprising finding, for in Thomson's model the positive charge of the atom was so diffuse (spread out) that the positive *α*particles were expected to pass through with very little deflection.



Sulfure de zinc
is a substance that glows
when α particles fall on it

To explain the results of the α-scattering experiment, Rutherford devised a new model of atomic structure, suggesting **that most of the atom must be empty space**.

- This structure would allow most of the αparticles to pass through the gold foil with little or no deflection.

- The atom's positive charges are all concentrated in the ***nucleus***, *a dense central core within the atom.*
- Whenever anαparticle came close to a nucleus in the scattering experiment, it experienced a large **repulsive force** and therefore a large deflection.
- Moreover, anαparticle traveling directly toward a nucleus would experience an **enormous repulsion** that could completely reverse the direction of the moving particle.

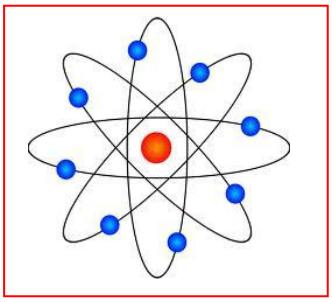
The positively charged particles in the nucleusare called ***protons***. In separate experiments, it was found that the charge of each proton has the same *magnitude* as that of an electron.

Modern measurements show that an atom has a diameter of roughly 10^{-10} m and that a nucleus has a diameter of about 10^{-15} m.

$$\boxed{q_P = +1.6\times10^{-19} c}$$

$$\boxed{m_P = 1.6726\times10^{-27} Kg}$$

Rutherford was able to determine the magnitudes of the protons on the atomic nuclei. The picture of atomic structure that he developed is called the **Rutherford model of the atom**.



The Neutron

Rutherford's model of atomic structure left one major problem unsolved. It was known that hydrogen, the simplest atom, contains only one proton and that the helium atom contains two protons. Therefore, the ratio of the mass of a helium atom to that of a hydrogen atom should be 2:1. (Because electrons are much lighter than protons, their contribution can be ignored.) In reality, however, the ratio is 4:1. Rutherford and others postulated that there must be another type of subatomic particle in the atomic nucleus; the proof was provided by another English physicist, **James Chadwick,** in **1932**.

When Chadwick bombarded a thin sheet of beryllium withαparticles, a very high energy adiation similar to γrays was emitted by the metal.Later experiments showed that the rays actually consisted of **electrically neutralparticles having a mass slightly greater than that of protons.** Chadwick named these particles **neutrons.**

The mystery of the mass ratio could now be explained. In the helium nucleusthere are two protons and two neutrons, but in the hydrogen nucleus there is only oneproton and no neutrons; therefore, the ratio is 4:1.

There are other subatomic particles, but the electron, the proton, and the neutron are the three fundamental components of the atom that are important in chemistry.

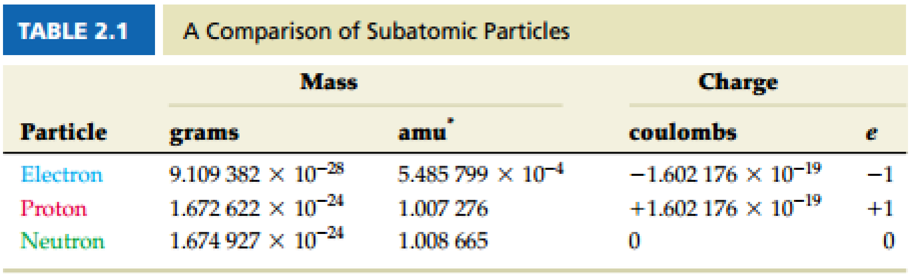


TABLE 2.1 A Comparison of Subatomic Particles

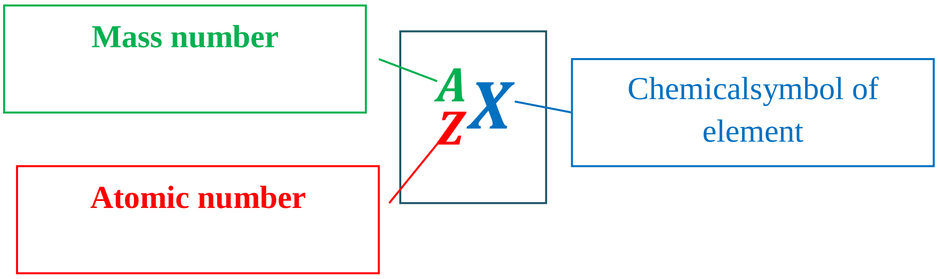
	Mass		Charge	
Particle	**grams**	**amu***	**coulombs**	***e***
Electron	$9.109\,382 \times 10^{-28}$	$5.485\,799 \times 10^{-4}$	$-1.602\,176 \times 10^{-19}$	−1
Proton	$1.672\,622 \times 10^{-24}$	1.007 276	$+1.602\,176 \times 10^{-19}$	+1
Neutron	$1.674\,927 \times 10^{-24}$	1.008 665	0	0

V- Presentation and characteristics of the atom

1. Symbol

Chemical elements are represented by a chemical symbol, with the atomic number and mass number sometimes affixed as indicated below.

A **nuclide** is an atom characterized by a definite atomic number and mass number. The shorthand notation for any nuclide consists of the symbol of the element with the atomic number written as a subscript on the left and the mass number as a superscript on the left.



2. Atomic number Z

All atoms can be identified by the number of protons and neutrons they contain. The number of protons in the nucleus of each atom of an element is called the **atomic number (Z).**

In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely by its atomic number.

3. Mass number A

The **mass number (A)** is the total number of neutrons and protons present in the nucleus of an atom of an element. Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contain both protons and neutrons. In general, the mass numberisgiven by

mass number = number of protons + number of neutrons

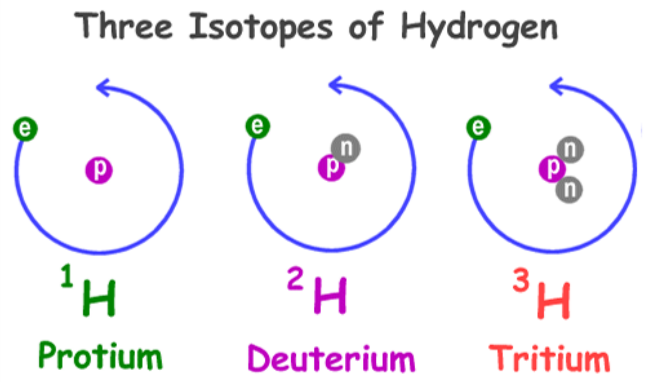
= atomic number + number of neutrons

The number of neutrons in an atom is equal to the difference between the mass number and the atomic number, or **(A - Z).**

VI-Isotopic and relative abundance of different isotopes

The term `isotope´ is derived from the Greek (meaning equal place): the various isotopes of an element occupy the same position in the periodic table. Isotopes of an element can either be stable or unstable (radiogenic).

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons.



The percentage of a given isotope in the naturally occurring sample of an element is called **isotopic abundance (e%)**.

You calculate the **atomic mass** of an element by multiplying each isotopic mass **M_e** by its fractional abundance**e%** and summing the values.

$$\textbf{atomic mass} = \textbf{average mass} = \frac{\sum \mathbf{M_e} \times \mathbf{e\%}}{\mathbf{100}}$$

Execise 3.

Chlorine has two naturally occurring isotopes: ${}^{35}_{17}\mathrm{Cl}$with a natural abundance of 75.77%and an isotopic mass of 34.969 amu, and ${}^{37}_{17}\mathrm{Cl}$with a natural abundance of 24.23% and an isotopic mass of 36.966 amu. What is the atomic mass of chlorine?

Isobars: are the atoms of different elements with the same mass number but different atomic numbers. In other words, isobars have different number of protons, neutrons and electrons but the sum of protons and neutrons (i.e., number of nucleons) is same.

Example: ${}^{40}_{18}\mathrm{Ar}$, ${}^{40}_{19}\mathrm{K}$and ${}^{40}_{20}\mathrm{Ca}$

Isotones: Isotones are the atoms of different elements with the same number of neutrons but different mass numbers.

Example: ${}^{30}_{14}\mathrm{Si}$, ${}^{31}_{15}\mathrm{P}$and ${}^{32}_{16}\mathrm{S}$

Execise 3.

The atomic mass of Ga is 69.72 amu. There are only two naturally occurring isotopes of gallium: ${}^{69}\mathrm{Ga}$, with a mass of 69.0 amu, and ${}^{71}\mathrm{Ga}$, with a mass of 71.0 amu. The natural abundance of the ${}^{69}\mathrm{Ga}$ isotope is approximately:**a**. 15% ; **b**. 30% ;**c**. 50% ;**d**. 65% or **e**. 80%.

VII- Mass spectrometry: Bainbridge spectrograph

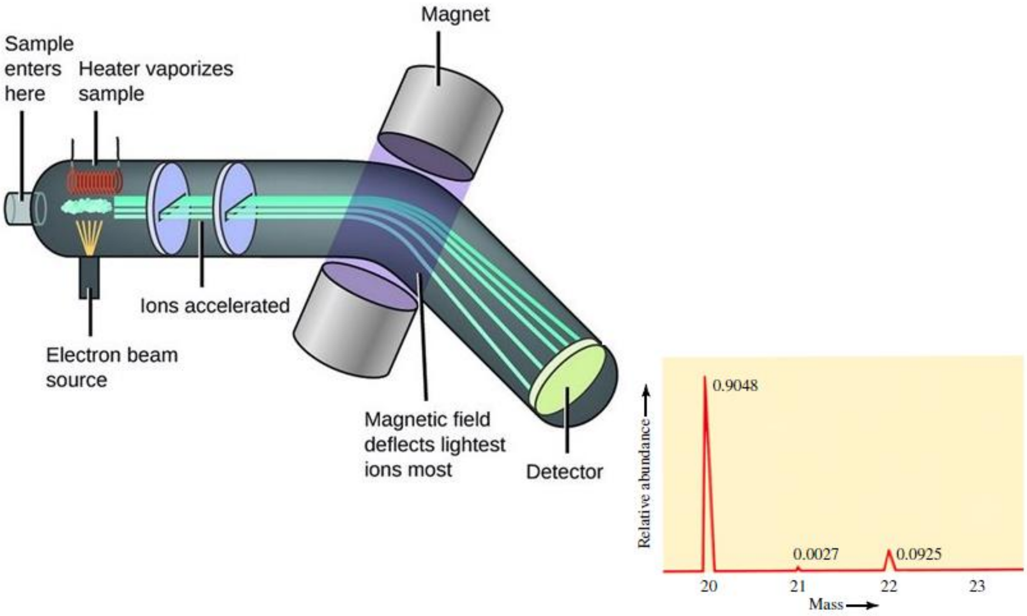
(Separation of isotopes and determination of the atomic mass and the average mass of an atom)

The most direct and most accurate method for determining atomic and molecular masses is mass spectrometry.

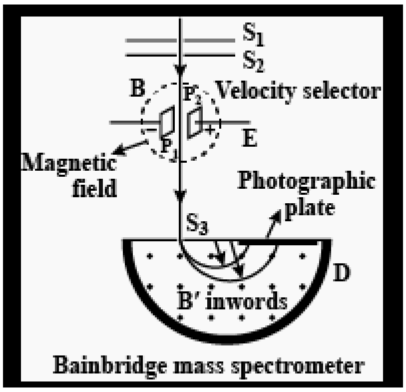
In a mass spectrometer, a gaseous sample is bombarded by a stream of high-energy electrons.Collisionsbetween the electrons and the gaseous atoms (or molecules) produce positive ions by dislodging an electron from each atom or molecule.

$$\mathbf{M + e^- \rightarrow M^{\bullet +} + 2e^-}$$

1. **Ion Source**: All mass spectrograph starts with an ion source to be detected. The ions are produced either by electron-bombardment of gases or by heating the suitable coated filaments.



2. **Energy, Momentum and Velocity Filter**: The velocity selector allows the ions of a particular velocity to come out of it, by the combined action of an electric and a magnetic field. The velocity selector consists of two plane parallel plates **P1** and **P2**, which produces a uniform electric field **E** and an electromagnet, to produce uniform magnetic field **B** (represented by the dotted circle). These two fields are so adjusted that the deflection produced by one field is nullified by the other, so that the ions do not suffer any deflection within the velocity selector.



Bainbridge mass spectrometer

The force exerted by the electric field is equal to **q.E** and the force exerted by the magnetic field is equal to **B.q.v** where v is the velocity of the positive ion.

$$F_e = F_m \Rightarrow qE = qvB \Rightarrow \mathbf{v = \frac{E}{B}}$$

Where **E** and **B** are the electric field intensity and magnetic induction respectively and **q** is the charge of the positive ion.

3. **Evacuated Chamber**: These positive ions having the same velocity are subjected to another strong uniform magnetic field of induction **B′** at right angles to the plane of the paper acting inwards. These ions are deflected along circular path of radius **R** and strike the photographic plate. The force due to magnetic field **B′.q.v** provides the centripetal force mv^2/R.

$$q\,v\,B' = \frac{mv^2}{R} \Rightarrow \frac{q}{m} = \frac{v}{RB'} \Rightarrow \boxed{\frac{\mathbf{q}}{\mathbf{m}} = \frac{\mathbf{E}}{\mathbf{BB'R}}}$$

4. **Detector:** It may be a photographic plate or an electrometer. The distance between the opening of the chamber and the position of the dark line gives the diameter 2R from which radius R can be calculated.

Ions of smaller e/m ratio trace a wider curve than those having a larger e/m ratio, so that ions with equal charges but different masses are separated from one another.

Exercise 4:

Bainbridge mass spectrometer was used to separate two ions, one of which was oxygen ^{16}O and the other was unknown. The velocity of the ions was 200 km/s and they are deflected by a magnetic fiel of 0.3 Tesla. The unknown ion is deflected along circular path of radius R equals twice the ^{16}Oradius. The distance between thetwo contact spots of ions on the screen is 1.38 cm. what is the mass of unknown ion?

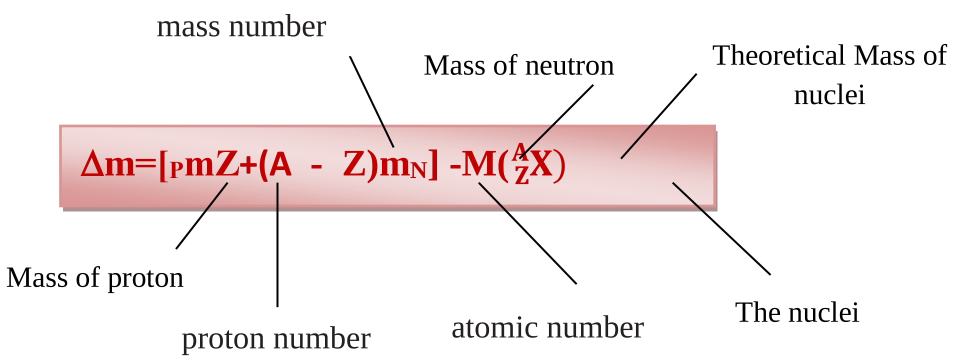
VIII- Energy of connection and cohesion of the nuclei

In nuclear reactions, matter is transformed into energy. The relationship between matter and energy is given by **Albert Einstein's** (theory of relativity) now famous equation:

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

ΔE stands for energy, **Δm** stands for mass defect, and **$c= 3\times 10^8$ m/s**, the constant that relates the two, is the speed of light.

This equation tells us that the amount of energy released when matter is transformed into energy is the product of the mass of matter transformed and the speed of light squared. And the **Mass Defect**is given by:



$$\Delta m=[{}_{P}mZ+(A - Z)m_N]-M({}^{A}_{Z}X)$$

IX- Stability of atomicnuclei

The energy required to break down a nucleus into its component nucleons is called the ***nuclear binding energy***.

Example: what is the nuclear binding energy of iron$^{56}_{26}$Fewhen m_p = 1.0072 uma ; m_N= 1.0086uma ; M(Fe) = 55.9375uma.

- Nuclear binding energies are usually expressed in terms of **kJ/mole of nuclei** or **MeV's/nucleon**

- **Megaelectronvolt(MeV)**

An electronvolt (symbol eV) is the measure of an amount of kinetic energy gained by a single electron accelerating from rest through an electric potential difference of one volt in vacuum.

$$E=q\times U$$

$$1ev = 1{,}6\times10^{-19}\ c \times 1\ volt \Rightarrow 1ev = 1{,}6\times10^{-91}\ c\times volt$$

$$\boxed{1\ ev = 1{,}6\times10^{-19}\ joule}$$

$$\boxed{1\ Mev = 10^{6} ev}$$

The stability of the nucleus of an atom can be determinedby calculating the **average binding energya**, defined as follows:

$$a = \frac{\Delta E}{A}$$

The greater the average binding energy, the more stable the element

- **The energy equivalent of 1 amu**

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

$$\Delta E= 1\times1.66\times10^{-27}\times(3\times10^{8})^{2}$$

$$\Delta E=14.94\times10^{-11}J \qquad J =(Kg.m^{2})/s^{2}$$

$$\Delta E=\frac{14{,}94\times10^{-11}}{1{,}6\times10^{-19}} = 9{,}31\times10^{8}ev$$

$$\boxed{\Delta E=931\ Mev}$$

$$\boxed{1uma \longrightarrow 931Mev}$$

Exercise 5: Find the mass defect of a copper-63 nucleus if the actual mass of a copper-63 nucleus is 62.91367 amu. (m_p = 1.00727 amu ; m_N = 1.00866 amu)

- Find the composition of the copper-63 nucleus and determine the combined mass of its components.
- Determine the binding energy of the copper-63 atom.
- Compare the stability of the copper-63 nucleus with the iron-56 nucleus.

CHAPTER 3.

RADIOACTIVITY – NUCLEAR REACTIONS

Chapter contents

- **Natural radioactivity (α, β and γ radiation),**
- **Artificial radioactivity and nuclear reactions,**
- **Kinetics of disintegration radioactive,**
- **Radioactivity Applications.**

I- Introduction

In **1895**, the German physicist **Wilhelm Röntgen**noticed that cathode rays caused glass and metals to emit very unusual rays. This highly energetic radiation penetrated matter, darkened covered photographic plates, and caused a variety of substances tofluoresce. Because these rays could not be deflected by a magnet, they could not containcharged particles as cathode rays do. Röntgen called them X rays.

After that, **Antoine Becquerel** **(1896)**, a professor of physics in Paris, began to study fluorescent properties of substances. He foundthaturanium compound gaveoffrays with high energy and could not be deflected by a magnet, but they differed from X rays because they were generated spontaneously.

One of Becquerel's students, **Marie Curie**, suggested the name **radioactivity** to describe this spontaneous emission of particles and/or radiation. Consequently, any element that spontaneously emits radiation is said to be radioactive.

In chemical reactions, only the outer electrons of the atoms are disturbed. The nuclei of the atoms are not affected. In nuclear reactions, however, the nuclear changes that occur are independent of the chemical environment of the atom.We will look at two types of nuclear reactions.

- One type is **radioactive decay,** the process in which a nucleus spontaneously disintegrates, giving off radiation. The radiation consists of one or more of the following, depending on the nucleus: electrons, nuclear particles (such as neutrons), smaller nuclei (usually helium-4 nuclei), and electromagneticradiation.

- The second type of nuclear reaction is a **nuclear bombardment reaction,** a nuclear reaction in which a nucleus is bombarded, or struck, by another nucleus or by a nuclear particle. If there is sufficient energy in this collision, the nuclear particles of the reactants rearrange to give a product nucleus or nuclei.

II- Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 270 are stable.

- Stable isotopes have a neutron-to-proton ratio (n/p) less than <1.

- All elements with $Z > 83$ are unstable and radioactive.
- The greater the average binding energy, the more stable the element

This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

MagicNumbers

The "magicnumbers" are natural occurrences in isotopes that are particularly stable. In some cases there the isotopes canconsist of magicnumbers for both protons and neutrons; thesewouldbecalled **double magicnumbers**. The magicnumbers are:

- proton: 2, 8, 20, 28, 50, 82, 114
- neutron: 2, 8, 20, 28, 50, 82, 126, 184

Also, thereis the concept that isotopes consist a combination of even-even, even-odd, odd-even, and odd-odd are all stable. There are more nuclides that have acombination of even-eventhanodd-odd.

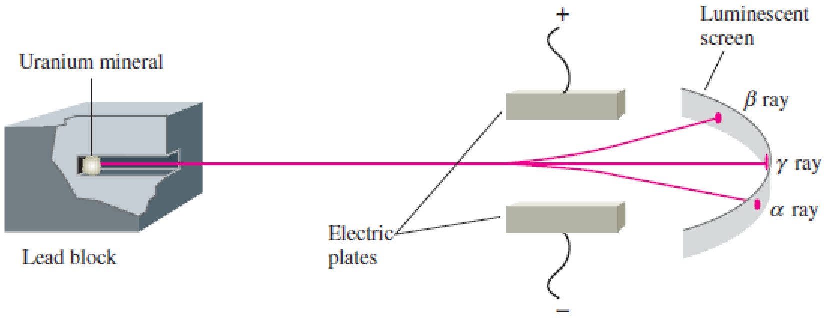
Table 1: Distribution of Stable and Unstable Isotopes based on Neutron and Proton Numbers

Proton number (Z)	Neutron Number	# of stable Isotopes
Even	Even	163
Even	Odd	53
Odd	Even	50
Odd	Odd	4

Although rare, four stable odd-odd nuclides exist : $^{2}_{1}\mathrm{H},\ ^{6}_{3}\mathrm{Li},\ ^{10}_{5}\mathrm{B},\ ^{14}_{7}\mathrm{N}$

III- Natural radioactivity (α, β and γ radiation)

The radiation from uranium minerals was later shown to be separable by electric (and magnetic) fields into three types, alpha (α), beta (β), and gamma (γ) rays.



1. **Alpha rays**: bend away from a positive plate and toward a negative plate, indicating that they have a positive charge; they are now known to consist ofhelium-4 nuclei (nuclei with two protons and two neutrons). For energeticreasonsα- decayhappensonly for heavy nuclides with a > 170 and $Z > 70$ according to :

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

2. **Beta rays**: bend in the opposite direction, indicating that they have a negative charge; they are now knownto consist of high-speed electrons. In a beta decay a neutron in the nucleus changes into a proton (β −-decay)

$${}_{0}^{1}n \quad \longrightarrow \quad {}_{1}^{1}P \; + \; {}_{-1}^{0}\beta$$

$${}_{Z}^{A}X \quad \longrightarrow \quad {}_{Z+1}^{A}Y \; + \; {}_{-1}^{0}\beta$$

First the emitted particles were called beta particles; later they were shown to be electrons. The emitted electron is not one of the orbital electrons of the atom. The new particle was called **neutrino**.

Another beta decay process is the so called β^+ decay in which a **positron** is emitted. Or a proton changes into a neutron (β^+ decay). Z and N each change by one unit but A does not change.

$${}_{1}^{1}P \;\rightarrow {}_{0}^{1}n \quad + {}_{+1}^{0}\beta$$

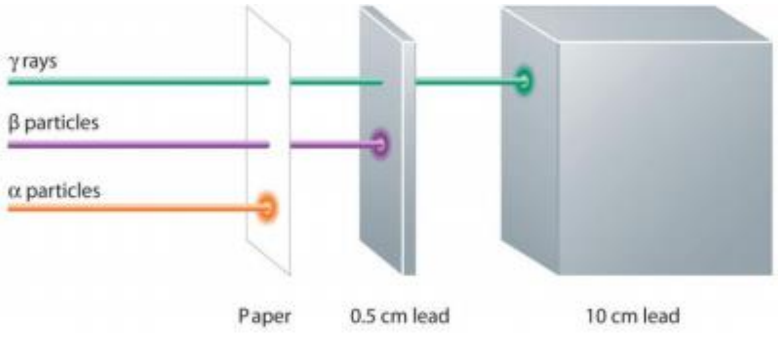
$${}_{Z}^{A}X \;\rightarrow {}_{Z-1}^{A}Y \quad + {}_{+1}^{0}\beta$$

The positron is the antiparticle of the electron. The only change of an anti particle is its charge. The β^+-decay is only possible if the available energy is greater than 1 MeV.

3. **Gamma rays**: are unaffected by electric and magnetic fields: they have been shown to be a form of electromagnetic radiation that is similar to X rays, except they are higher in energy with shorter wavelengths.

   Following alpha or beta decay, the final nucleus may be left in an **excited state**. Just as an atom does, the nucleus will reach its ground state after emitting one or more photons, known as **nuclear gamma rays**.

A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them.



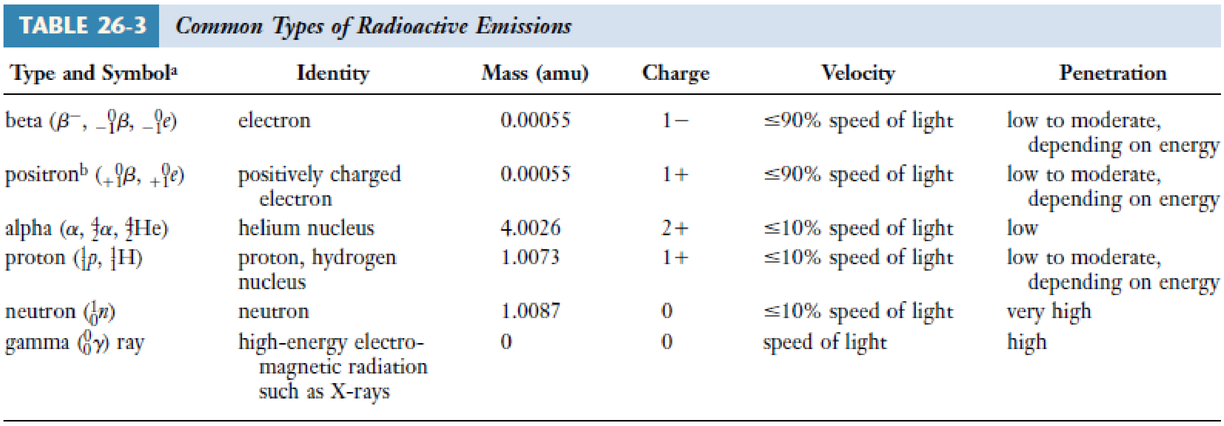


TABLE 26-3 *Common Types of Radioactive Emissions*

Type and Symbol[a]	Identity	Mass (amu)	Charge	Velocity	Penetration
beta (β^-, ${}_{-1}^{0}\beta$, ${}_{-1}^{0}e$)	electron	0.00055	1−	≤90% speed of light	low to moderate, depending on energy
positron[b] (${}_{+1}^{0}\beta$, ${}_{+1}^{0}e$)	positively charged electron	0.00055	1+	≤90% speed of light	low to moderate, depending on energy
alpha (α, ${}_{2}^{4}\alpha$, ${}_{2}^{4}\mathrm{He}$)	helium nucleus	4.0026	2+	≤10% speed of light	low
proton (${}_{1}^{1}p$, ${}_{1}^{1}\mathrm{H}$)	proton, hydrogen nucleus	1.0073	1+	≤10% speed of light	low to moderate, depending on energy
neutron (${}_{0}^{1}n$)	neutron	1.0087	0	≤10% speed of light	very high
gamma (${}_{0}^{0}\gamma$) ray	high-energy electromagnetic radiation such as X-rays	0	0	speed of light	high

Exercise 1.

1- Write the nuclear equation for the radioactive decay of radium-226 by alpha decay to give radon-222. Aradium-226 nucleus emits one alpha particle, leaving behind a radon-222 nucleus.

2- Technetium-99 is a long-lived radioactive isotope of technetium. Each nucleus decays by emitting one betaparticle. Whatis the product nucleus?

3- Calculate the number of α and β particules emitting during the decay of ${}_{93}^{273}\mathrm{Np}$ to ${}_{87}^{221}\mathrm{Fr}$.

4- An alpha particle is accelerated to 23.1 MeV per particle. What is this energy in kJ/mol?

IV-Artificial radioactivity and nuclear reactions

The first man-made nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

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

The ${}_{8}^{17}\mathrm{O}$ and ${}_{1}^{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

Writing a nuclear equation differs somewhat from writing equations for chemical reactions. In addition to writing the symbols for various chemical elements, we must also explicitly indicate protons, neutrons, and electrons. In fact, we must show the numbers of protons and neutrons present in every species in such an equation.

The Symbols for elementary particles are as follows

$^{1}_{1}P$ or $^{1}_{1}H$	$^{1}_{0}n$	$^{0}_{-1}e$ or $^{0}_{-1}\beta$	$^{0}_{+1}e$ or $^{0}_{+1}\beta$	$^{4}_{2}He$ or $^{1}_{1}\alpha^{2}_{1}H$	$^{2}_{1}d$
Proton	neutron	electron	positon	α particule	duteron

The nuclear equation is not balanced in the usual chemical sense because the kinds of nuclei are not the same on both sides of the arrow. Instead, a nuclear equation is balanced when the sums of the nucleons are the same on both sides of the equation and when the sums of the charges on the nuclei and any elementary particles (protons, neutrons, and electrons) are the same on both sides.

Note also that we are concerned only with charges on elementary particles and on nuclei when we write nuclear equations, not with ionic charges on atoms.

Exercise 2.

- Write the nuclearequations for the followingbombardmentreactions.

a. $^{45}_{21}Sc\ (n,\alpha)\ ^{42}_{19}K$; **b.** $^{63}_{29}Cu\ (p,n)\ ^{63}_{30}Zn$

c. $^{14}_{6}C\ (\beta^{-})\ ^{14}_{7}N$; **d.** $^{252}_{98}Cf(n)^{142}_{56}Ba,\ ^{106}_{42}Mo$

- Write the abbreviated notations for the followingbombardmentreactions.

a. $^{26}_{12}Mg + ^{2}_{1}H \longrightarrow ^{24}_{11}Na + ^{4}_{2}He$

b. $^{16}_{8}O + ^{1}_{0}n \longrightarrow ^{16}_{7}N + ^{1}_{1}p$

a. $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$

b. $^{63}_{29}Cu + ^{4}_{2}He \longrightarrow ^{66}_{31}Ga + ^{1}_{0}n$

a. $^{31}_{14}Si \longrightarrow ^{31}_{15}P + ?$

- Fill in the missing parts of the following reactions.

a. $^{6}_{3}Li + ^{1}_{0}n \longrightarrow ? + ^{3}_{1}H$

b. $^{232}_{90}Th(?, n)^{235}_{92}U$

a. $^{27}_{13}Al + ^{3}_{1}H \longrightarrow ^{27}_{12}Mg + ?$

b. $^{12}_{6}C(^{3}_{1}H, ?)^{14}_{6}C$

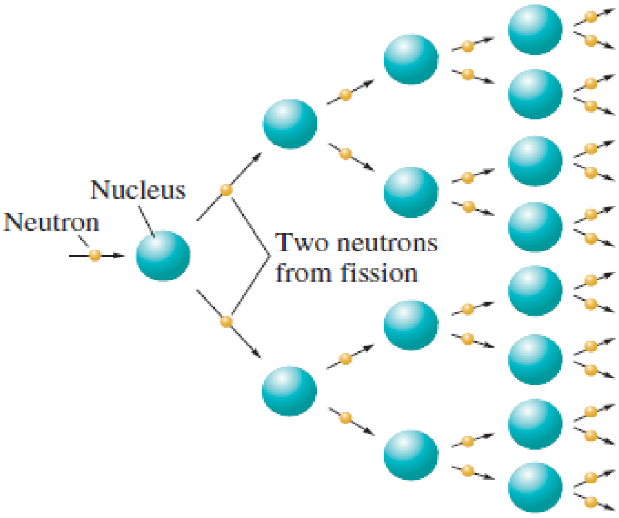
a. $^{31}_{14}Si \longrightarrow ^{31}_{15}P + ?$

Transmutationisthe change of one element to another by bombarding the nucleus of the element with nuclear particles or nuclei.

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

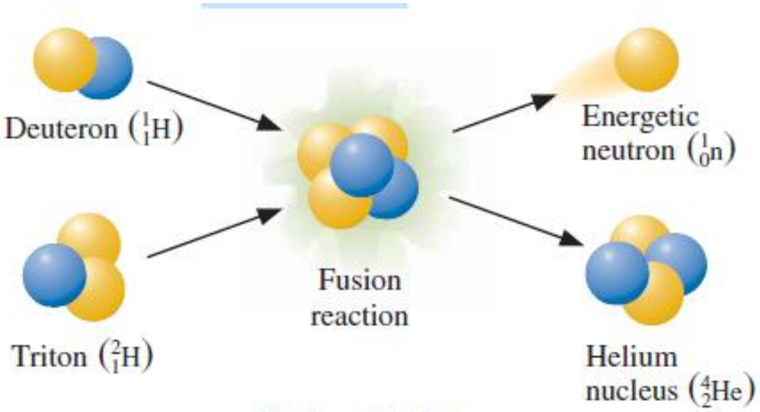
Nuclear fission is a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released. For example, uranium-235 isemployed in nuclear power plants to generate electricity. One way of nuclear fission of uranium is represented by the following equation:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\,{}^{1}_{0}n + \text{طاقة}$$



Nuclear fusion is a nuclear reaction in which light nuclei combine to give a stabler, heavier nucleus plus possibly several neutrons, and energy is released. An example of nuclear fusion is :

$$^{2}_{1}\mathrm{H} + {}^{3}_{2}\mathrm{He} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{1}\mathrm{H}$$



Nuclear Fusion

Exercise 3.

Identify each of the following reactions as fission, fusion, a transmutation, or radioactive decay.

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

b. $^{14}_{6}\mathrm{C} \longrightarrow \,^{14}_{7}\mathrm{N} + \,^{0}_{-1}\mathrm{e}$

c. $^{1}_{0}\mathrm{n} + \,^{235}_{92}\mathrm{U} \longrightarrow \,^{140}_{56}\mathrm{Ba} + \,^{93}_{36}\mathrm{Kr} + 3\,^{0}_{1}\mathrm{e}$

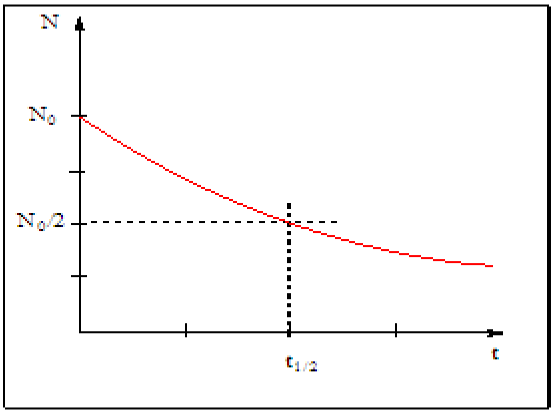
d. $^{14}_{7}\mathrm{N} + \,^{4}_{2}\mathrm{He} \longrightarrow \,^{17}_{8}\mathrm{O} + \,^{1}_{1}\mathrm{H}$

V- Kinetics of disintegration radioactive

Radionuclides have different stabilities and decay at different rates. Some decay nearly completely in a fraction of a second and others only after millions of years. The rates of all radioactive decays are independent of temperature and obey *first-order kinetics*.

The rate of a first-order process is proportional only to the concentration of one substance.

$$\Rightarrow \ln\frac{N_0}{N} = \lambda t \Rightarrow \mathbf{N(t)=N_0e^{-\lambda t}} \frac{dN}{dt} = -\lambda N$$



Here :

- N represents the amount of decaying radionuclide of interest remaining after sometime *t*, and

- N_0 is the amount present at the beginning of the observation.

- $\lambda$is the rateconstant, which is different for each radionuclide.

Because N_0/N is a ratio, N_0 and N can represent either molar concentrations of a reactantor masses of a reactant? We can write:

$$\mathbf{N} = \mathcal{N}\frac{\mathbf{m}}{\mathbf{M}} \Rightarrow m = m_0 e^{-\lambda t}$$

In nuclear chemistry, the decay rate is usually expressed in terms of the **half-life, *t*$_{1/2}$**, of the process. This is the amount of time required for half of the original sample to react.For a first-order process, $t_{1/2}$ is given by the equation:

$$\frac{N_0}{2} = N_0 e^{-\lambda t_{1/2}} \quad \Rightarrow \quad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

Exercise 4.

The decay constant for the beta decay of $^{99}_{43}\mathrm{Tc}$ is 10^{-13} s^{-1}. What is the half-life of this isotope in year?

1- Activity, the Rate of Decay

The Rate of Decay means the number of decays per unit time. We define activity A to be the rate of decay expressed in decays per unit time. In equation form, this is :

$$A = \lambda N \Rightarrow A_{(t)} = A_0 e^{-\lambda t}$$

The **becquerel (Bq)** is the SI unit for measuring the number of nuclear disintegrations occurring per second in a sample: The **curie (Ci)** and **millicurie (mCi)** also measure disintegrations per unit time, but they are far larger units than the becquerel and are more often used, particularly in medicine and biochemistry.

One curie is the decay rate of 1 g of radium, equal to **3.7 * 10^{10} Bq**:

$$\mathbf{1\ Bq = 1\ disintegration/s \Rightarrow 1\ Ci = 3.7 * 10^{10} Bq = 3.7 * 10^{10} disintegrations/s}$$

Exercise 5.

A 1 mg sample of technetium-99 has an activity of 1.7 × 10^{-5}Ci, decaying by beta emission. What is the decay constant for $^{99}_{43}\mathrm{Tc}$.

2- Decayenergy

The decay energy is the energy change of a nucleus having undergone a radioactive decay. The energy difference of the reactants is often written as :

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

Where :

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

Exercise 6.

- How much energy (in kj/mol) is released by the fission of uranium-235 to form barium-142 and krypton-91? The atomic masses are ^{235}U (235.0439 amu), ^{142}Ba (141.9164 amu), ^{91}Kr (90.9234 amu) and n (1.00866 amu).

$$^{1}_{0}n + ^{235}_{92}U \longrightarrow ^{142}_{56}Ba + ^{91}_{36}Kr + 3\,^{1}_{0}n$$

- Calculate the amount of energy released (in kj/mol) for the fusion reaction of ^{1}H and ^{2}H atom to yield a ^{3}He atom.

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

The atomic masses are ^{1}H (1.007 83 amu), ^{2}H (2.014 10 amu), and ^{3}He (3.016 03 amu).

Exercise 7.

- Does the following nuclear reaction absorb or release energy:

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

- Calculate the value of this energy in megaelectron volts.

Masses are given in amuunits: ^{14}N = 14.00754 ;^{4}He = 4.00388 ; ^{17}O= 17.0045 ; ^{1}H = 1.00783

VI- Radioactivity Applications

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is radiometric dating and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization.

For example, F-18 is produced by proton bombardment of ^{18}O ($^{18}_{8}\mathrm{O} + ^{1}_{1}\mathrm{p} \longrightarrow ^{18}_{9}\mathrm{F} + ^{1}_{0}\mathrm{n}$) and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called radiocarbon dating or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{13}_{6}C$, which constitutes about 99% of the carbon on earth; $^{13}_{6}C$, about 1% of the total; and trace amounts of $^{14}_{6}C$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \longrightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}\mathrm{CO}_2$ to $^{12}_{6}\mathrm{CO}_2$depends on the ratio of $^{14}_{6}\mathrm{CO}$ to $^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\mathrm{CO}_2$ and $^{12}_{6}\mathrm{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}C$: $^{12}_{6}C$ratio found in a living plant is the same as the $^{14}_{6}C$: $^{12}_{6}C$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}C$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\mathrm{C} \longrightarrow ^{12}_{7}\mathrm{N} + ^{0}_{-1}\mathrm{e}$$

Thus, the $^{14}_{6}C$: $^{12}_{6}C$ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant).

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth).

Exercise 8:

A sample of uranium ore is found to contain 4.64 mg of 238U and 1.22 mg of 206Pb. Estimate the age of the ore. The half-life of ^{238}U is 4.51 × 10^9 years.

Medical Uses of Radioactivity

The origins of nuclearmedicine date to 1901, when the French physician Henri Danlos first used radium in the treatment of atuberculous skin lesion. Sincethat time, uses of radioactivity have become a crucial part of modern medical care, both diagnostic and therapeutic. Currentnucleartechniques canbegroupedintothree classes: (1) in vivo procedures, (2) therapeuticprocedures, and (3) imagingprocedures.

Exercise 9:

The "cobalt treatments" used in medicine to arrest certain types of cancer rely on the abilityof gamma rays to destroy cancerous tissues. Cobalt-60 decays with the emission of beta particlesand gamma rays, with a half-life of 5.27 years.Write the nuclearreaction.

- How much of a 3.42-g sample of cobalt-60 remains after 30.0 years?

Agricultural Uses

The pesticide DDT is toxic to humans and animals repeatedly exposed to it. DDT persists in the environment for a long time. It concentrates in fatty tissues. The DDT once used to control the screwworm fly was replaced by a radiological technique. Irradiating the male flies with gamma rays alters their reproductive cells, sterilizing them. When great numbers of sterilized males are released in an infested area, they mate with females, who, of course, produce no offspring. This results in the reduction and eventual disappearance of the population.

Labeled fertilizers can also be used to study nutrient uptake by plants and to study the growth of crops. Gamma irradiation of some foods allows them to be stored for longer periods without spoiling. For example, it retards the sprouting of potatoes and onions. In

1999, the FDA approved gamma irradiation of red meat as a way to curb food-borne illnesses. In addition to significantly reducing levels of *Listeria*, *Salmonella*, and other bacteria, such irradiation is currently the only known way to completely eliminate the dangerous strain of *Escherichia coli* bacteria in red meat. Absorption of gamma rays by matter produces no radioactive nuclides, so foods preserved in this way are *not* radioactive.

Industrial Uses

There are many applications of radiochemistry in industry and engineering. When great precision is required in the manufacture of strips or sheets of metal of definite thicknesses, the penetrating powers of various kinds of radioactive emissions are utilized. The thickness of the metal is correlated with the intensity of radiation passing through it. The flowModerate irradiation with gamma rays from radioactive isotopes has kept the strawberries at the right fresh for 15 days, while those at the left are moldy. Such irradiation kills mold spores but does no damage to the food. The fooddoes*not*become radioactive.
of a liquid or gas through a pipeline can be monitored by injecting a sample containing a radioactive substance. Leaks in pipelines can also be detected in this way. In addition to the 238Pu-based heart pacemaker already mentioned, lightweight, portable power packs that use radioactive isotopes as fuel have been developed for other uses. Polonium-210, californium-242, and californium-244 have been used in such generators to power instruments for space vehicles and in polarregions. These generators can operate for years with only a small loss of power.

CHAPTER 4.

ELECTRONIC STRUCTURE OF THE ATOM

Chapter contents

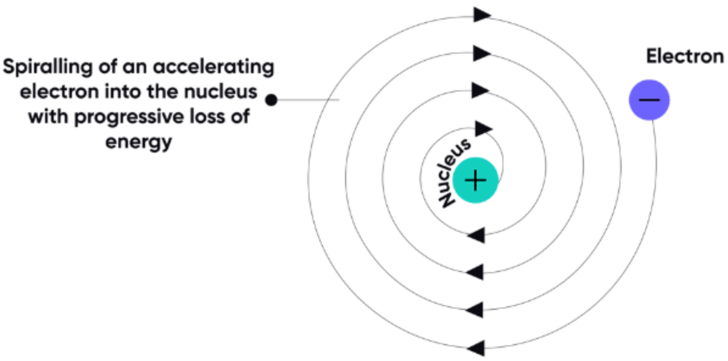
- **Wave-particle duality,**
- **Interaction between light and matter,**
- **Bohr's atomic model: hydrogen atom,**
- **The hydrogen atom in wave mechanics,**
- **Poly electronic atoms in wave mechanics**

I- Introduction

Rutherford’s atomic model failed to explain the stability of electrons in a circular path.

Drawbacks of Rutherford model

1. This was not according to the classical theory of electromagnetism proposed by Maxwell :Every accelerated charged particle must emit radiations in the form of electromagnetic waves and loses it total energy. Since energy of electrons keep on decreasing, so radius of the circular orbits should also decrease and ultimately the electron should fall in nucleus.But it never happens.



2. It could not explain the line spectrum of H-atom. According to this model the spectrum of atom must be continuous where as practically it is a line spectrum.

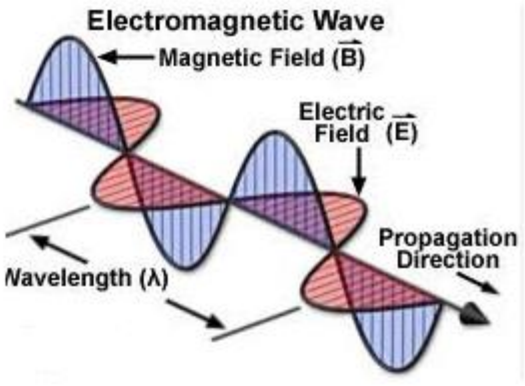
3. It did not explain how the e^- are distributed around the nucleus and what are the energies of these e^-.

II- Wave-particle duality

The main conclusion from both Planck’s and Einstein’s work was that the behavior of light and other forms of electromagnetic radiation is more complex than had been formerly believed. In addition to behaving as waves, light energy can also behave as small particles. First of all we need to understand what is electromagnetic radiation ?

1- Electromagnetic radiation

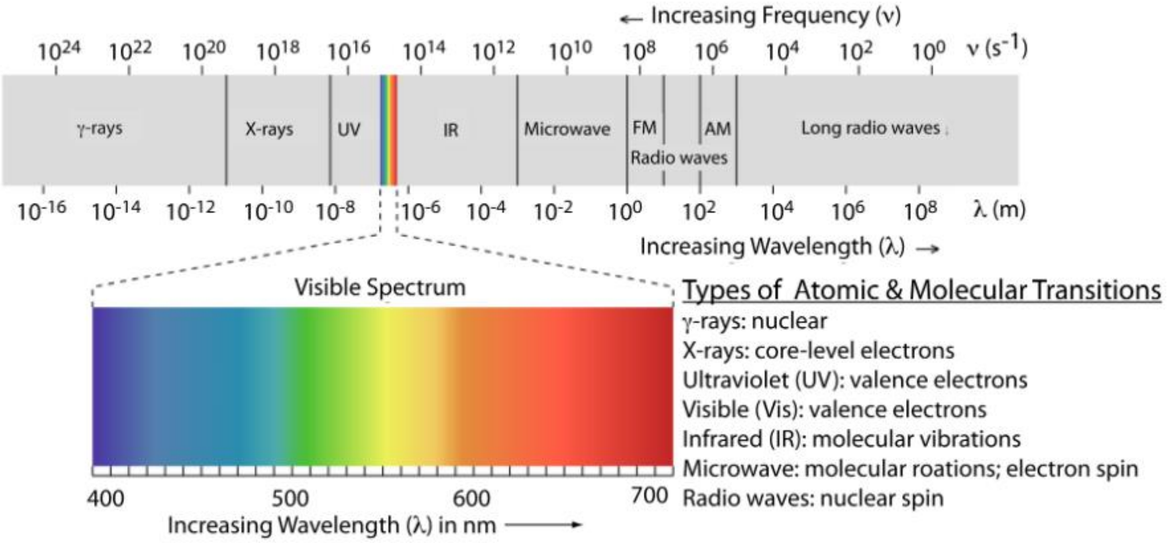
It consists of oscillating electric and magnetic fields, perpendicular to each other,that propagate in a vacuum with speed of light **$C = 3 \times 10^8$ m/s**. An electromagnetic wave is characterized by **wavelength, λ (Å)**, which is the distance between successive maxima.



Wavelength is inversely related to **frequency, ∂** , which refers to the number of wave cycles per second. The higher the frequency of the signal, the shorter the wavelength. The relationship between wavelength and frequency is :

$$\boxed{\partial = \frac{C(m/s)}{\lambda(m)}\,(S^{-1})}$$

Electromagnetic radiation is divide into different regions (**the electromagnetic spectrum**) based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons.



Types of Atomic & Molecular Transitions
γ-rays: nuclear
X-rays: core-level electrons
Ultraviolet (UV): valence electrons
Visible (Vis): valence electrons
Infrared (IR): molecular vibrations
Microwave: molecular roations; electron spin
Radio waves: nuclear spin

For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 µm = 10^{-6} m).

- Another unit useful unit is the **wavenumber**, $\bar{\partial}$, which is the reciprocal of wavelength :

$$\bar{\partial} = \frac{1}{\lambda}(\mathrm{m}^{-1}, \mathrm{cm}^{-1})$$

2- Quantum theory (Planck ; the Nobel Prize in Physics in 1918)

We have described light in terms of wave behavior. Under certain conditions, it is also possible to describe light as composed of *particles*, or **photons.**

Max Planck in **1900**, maked the assumption that each photon of light has aindividualamount (**a quantum**) of energy in the same way that matter does and was therefore ***quantifiable.*** The amount of energy possessed by a photon depends onthe frequency of the light. Planck wrote a mathematical equation involving a figure to represent these individual units of energy, which he called ***quanta***.

$$E = h\,\partial$$

where∂ is the frequency of the light and **h**is Planck's constant :

$$h = 6{,}62\times 10^{-34}\,\mathrm{j.s}$$

Exercise 1

The wavelengths of ultraviolet light of frequency $2.73 \times 10^{16}\ \mathrm{s}^{-1}$ and of yellow light of frequency $5.26 \times 10^{14}\ \mathrm{s}^{-1}$. Calculate the energy, in joules, of an individual photon of each. Compare these photons by calculating the ratio of their energies.

This exemple shows that a photon of ultraviolet light has more energy than a photon of yellow light (visible region).This is one reason why ultraviolet(UV) light damages your skin muchmore rapidly than visible light.

1- In case of light

The now-famous equation which had been proposed in **1905** by **Albert Einstein**(the 1921 Nobel Prize in physics) as part of his special theory of relativity. He extended Planck's idea that light behaves as though it were composed of ***photons***, each with a mass m_0 and particular amount of energy :

$$\mathbf{E = m_0\, c^2}$$

Since $E = h\partial$ then $h\partial = m_0c^2$ $\Rightarrow$ $h\frac{c}{\lambda} = m_0c^2$

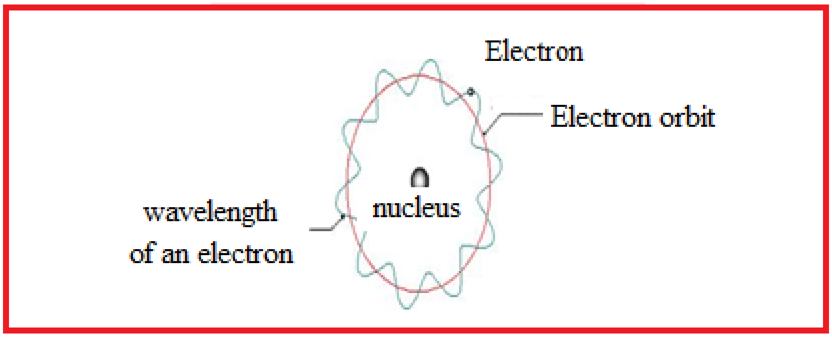
So it's possible to to derive a relationship between mass and wavelength:

$$\boxed{\lambda = \frac{h}{m_0 c}}$$

2- In case of matter

In **1924**, **Louis de Broglie** proposed that there is no fundamental difference in the behavior of energy and matter; on the atomic and subatomic level either may behave as if made of either particles or waves. This theory became known as the principleof*wave-particle duality*:

De Broglie suggested that a similar equation might be applied to an electron by replacing the speed of light (*c*) by the speed of the electron (*v*).



The resultant de Broglie equationthus allows calculation of a “wavelength” of an electron or of any other particle or object of mass ***m***moving at velocity ***v***:

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

Exemple 2

The mass of an electron is 9.11×10^{-31} kg and the velocity *v* of an electron in a hydrogen atom is 2.2×10^{6} m/s (about 1% of the speed of light). What is the wavelength of this electron ?

In **1913**,**Niels Bohr** assumed that the electron orbiting the nucleus in only certain stable orbits of specific energies and with stable wavelength.

Since the perimeter of the circle or circumference = **$2\pi r$** andit is surrounded by a natural number n of wavelength λ. So :

$$2\pi r = n\lambda \quad \text{and} \quad \lambda = \frac{h}{mv} \Rightarrow 2\pi r = \frac{nh}{mv} \Rightarrow \boxed{mvr = \frac{nh}{2\pi}}$$

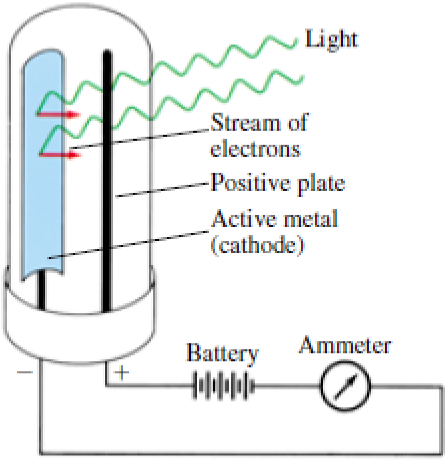
This equation is called **Bohr's quantum condition**.

III- Interaction between light and matter

1- The PhotoelectricEffect

In **1905**, the German-American physicist **Albert Einstein** used the theory to solve another mystery in physics, the photoelectric effect, a phenomenon in which electrons are ejected from the surface of certain metals exposed to light at least a certain minimum frequency, called the **threshold frequency**∂_0.

The apparatus for the photoelectric effect shown the negative electrode in the evacuated tube is made of a pure metal such as cesium. When light of a sufficiently high energy strikes the metal, electrons are knocked off its surface. They then travel to the positive electrode and form a current flowing through the circuit.



The important observations follow.

1. Electrons can be ejected only if the light is of sufficiently short wavelength and frequency more than threshold frequency $\partial_0 < \partial_1$ (has sufficiently high energy), no matter how long or how brightly the light shines. This wavelength limit is different for different metals.

2. The current (the number of electrons emitted per second) increases with increasing *brightness* (intensity) of the light. The current, however, does not depend on the color of the light, as long as the wavelength is short enough (has high enough energy).

when a photon falls on the surface of a metal, the entire photon's energy**E** is transferred to the electron. A part of this **energy E_0** (**work function or the binding energy of electrons**) is used to remove the electron from the metal atom's grasp and the rest is given to the ejected electron as **kinetic energy Ec**.

$$\Rightarrow \qquad E = E_C + E_0 \qquad\qquad \boxed{E - E_0 = E_C = 1/2\ mv^2}$$

where E_C is the kinetic energy of the ejected electron and $E_0$is called the **work functio**.

At the threshold frequency, ∂_0 electrons are just ejected and do not have any kinetic energy. Below this frequency,$\partial_0 > \partial_1$ there is no **electron emission**. Thus, the energy of a photon with this frequency must be the work function of the metal.

The more intense beam of light consists of a larger number of photons; consequently, it ejects more electrons from the metal's surface than the weaker beam of light. Thus, the more intense the light, the greater the number of electrons emitted by the target metal; the higher the frequency of the light, the greater the kinetic energy of the ejected electrons.

Exemple 3

a- What is the energy in joules and electron volts of a photon of 420-nm violet light?

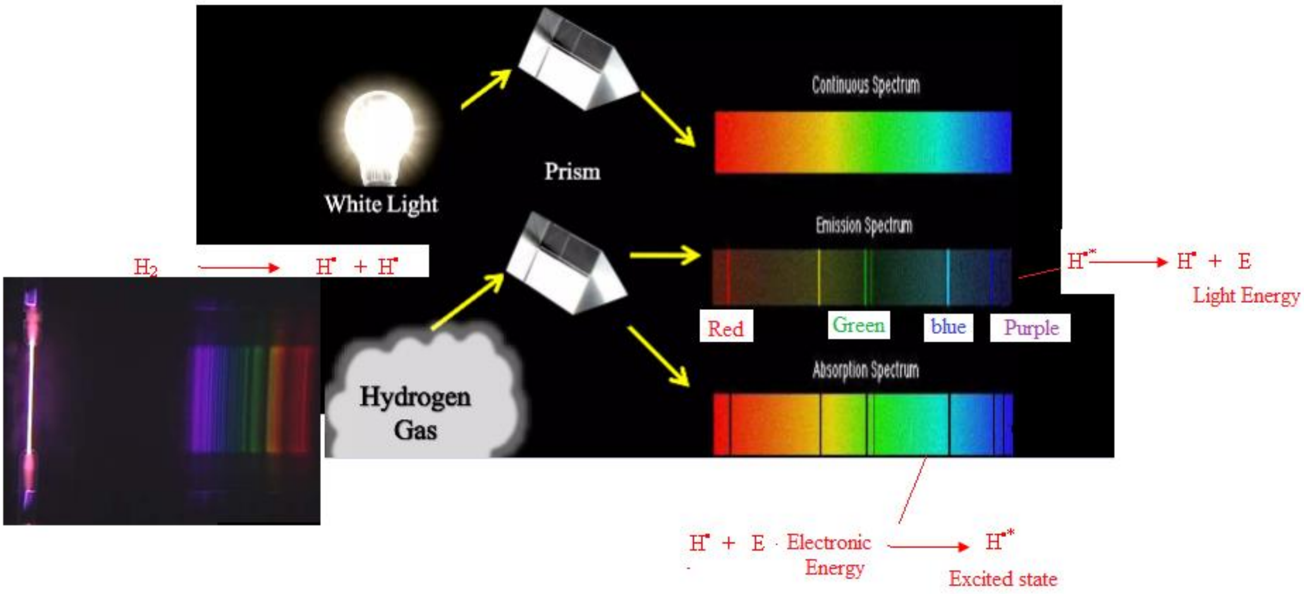
b- What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the binding energy (or work function) of electrons for calcium metal is 2.71 eV?

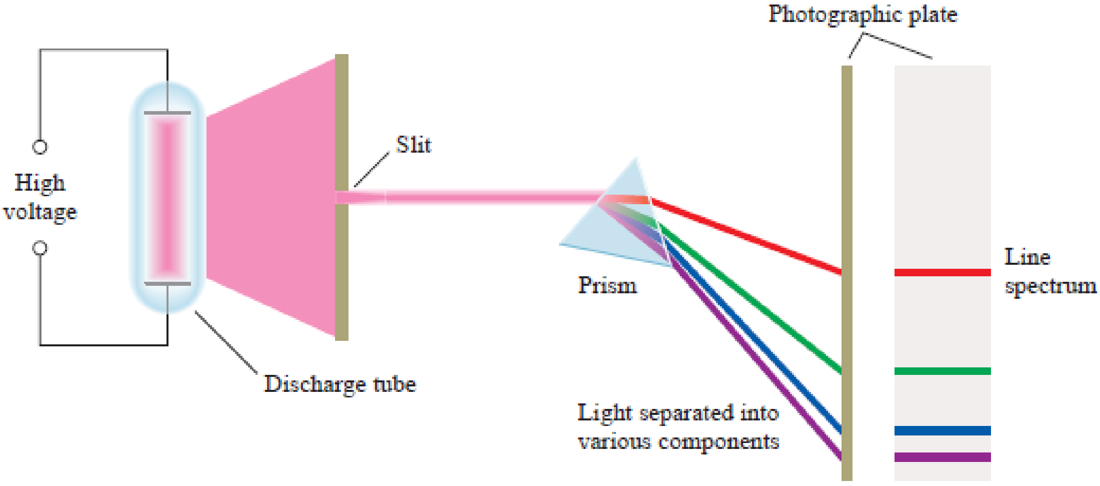
c- Calculate the velocity of the electrons ejected from calcium by 420-nm violet light.

d- Calculate the number of photons emitted per minute from 100W blue light bulb (λ = 420 nm)

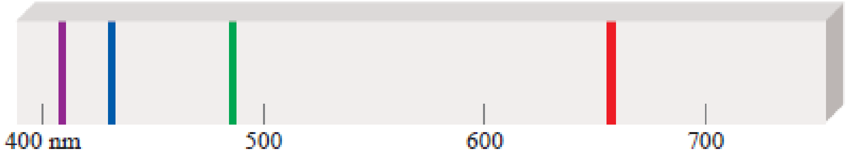
2- The spectrum of hydrogen atoms.

When an electric current is passed through hydrogen gas at very low pressures, several series of lines in the spectrum of hydrogen are produced. Theselineswerestudiedintenselybymanyscientists.





(a)



(b)

3- The line spectrum of the hydrogen

In the late nineteenth century, **Johann Balmer** (1825–1898) and **Johannes Rydberg** (1854–1919) showed that the wavelengths of the various lines in the hydrogen spectrum can be related by a mathematical equation:

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

WhereR_H, the Rydberg constant, hasthe value:

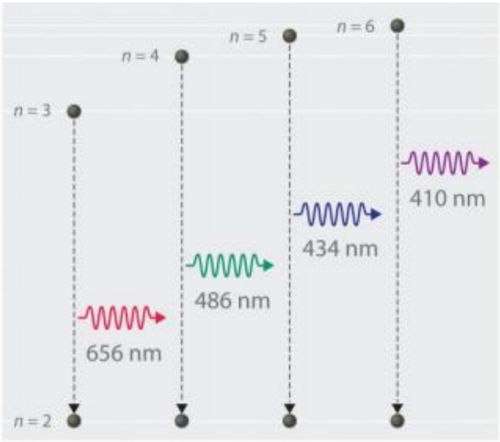
$$\mathbf{R_H = 1,09677\times 10^{5}\ cm^{-1}}$$

The number nis an integer called the **principal quantumnumber**; it has the values n= 1, 2, 3, ..

The general formula for the calculation of wave number $\bar{\partial}$of hydrogen spectral line emissions due to the transition of an electron from one orbit$\mathbf{n_1}$ to anotherorbit$\mathbf{n_2}$ is given by:

$$\bar{\partial} = \mathbf{R_H}\left(\frac{\mathbf{1}}{\mathbf{n_1^2}} - \frac{\mathbf{1}}{\mathbf{n_2^2}}\right) \mathbf{n_2} > \mathbf{n_1}$$

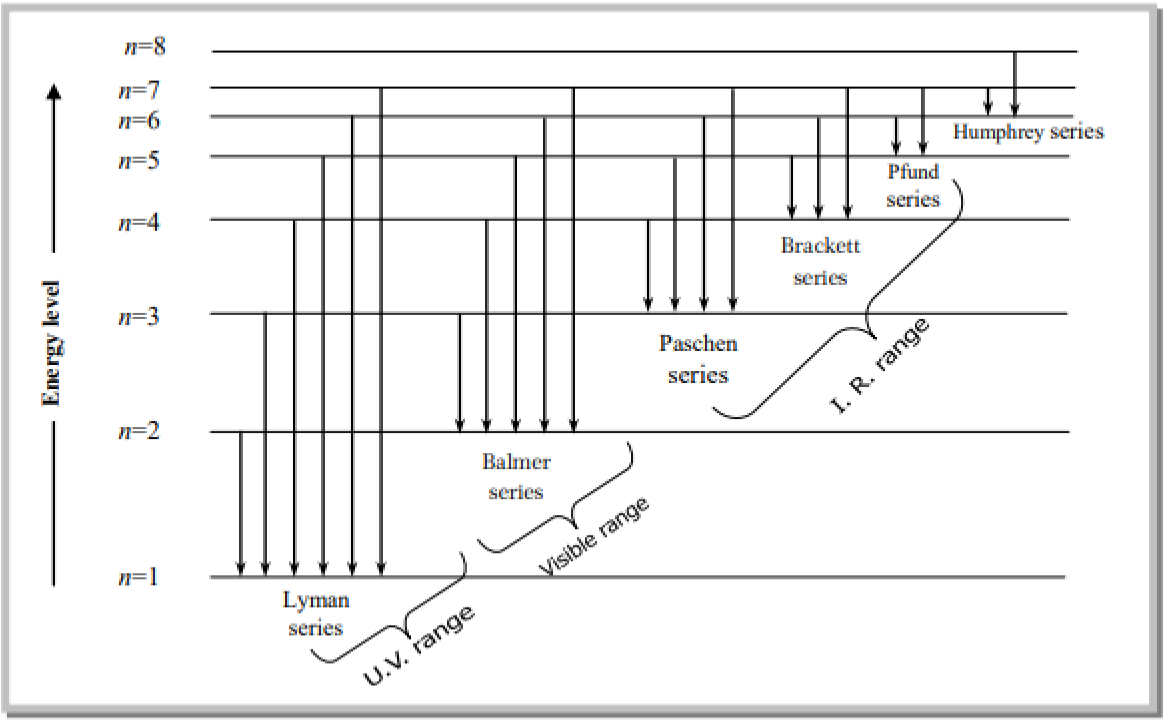
n_1 denotes the serie, while n_2 denotes a line within the serie.



The Balmer series is basically the part of the hydrogen emission spectrum responsible for the excitation of an electron from the second shell to any other shell. Similarly, other transitions also have their own series names. Some of them are listed below.

Table. The Various Series in Atomic Hydrogen Emission Spectrum.

Series	n_f	n_i	Spectrum Region
Lyman	**1**	2, 3, 4....	**Ultraviolet**
Balmer	**2**	3, 4, 5....	**Visible**
Paschen	**3**	4, 5, 6....	**Infrared**
Brackett	**4**	5, 6, 7....	**NeerInfrared**
Pfund	**5**	6, 7, 8....	**Far Infared**



The general formula for the calculation of wavenumber $\bar{\partial}$of hydrogen-like atomsspectral line emissionsis given by:

$$\bar{\partial} = \mathbf{R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) n_2 > n_1}$$

Not that, **hydrogen-like atoms**are any atom or ion that only have **one electron**. Examples all alkali metals such as **Rb and Cs**, singly ionized alkaline earth metals such as **Ca^+ and Sr^+** and other ions such as **He^+, Li^{2+}, and Be^{3+}** and isotopes of any of the above.

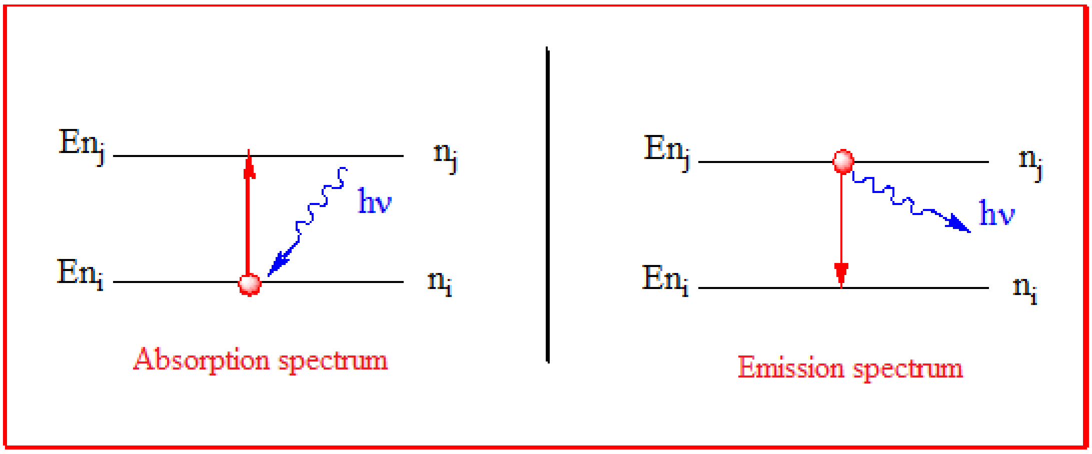
Exemple 4

1- Calculate the wavenumber of first line of Balmer series of hydrogen atom. What is the wavenumber of first line of Balmer series of ion Li^{3+}.

2- If the limit wavelength of the emitted spectral line for hydrogen atom is 187.5×10^{-9} m. what is the spectral series?

3- Emission energy

Light is emitted when the electron undergoes a transition from an orbit with **a higher value of n** (at a higher energy) to an orbit with **a lower value of n** (at lower energy) and versa.



The **energy gap**between these levels correspond to light in the visible portion of the electromagnetic spectrum and it is given by:

$$\Delta E = E_{final} - E_{initial}$$

In another side,

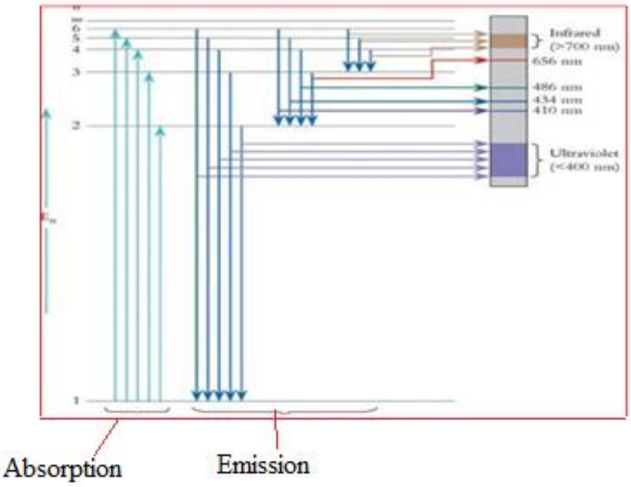
$$\Delta E = h\partial \qquad \text{and} \qquad \partial = \frac{c}{\lambda} = c\,\bar{\partial} \qquad \Rightarrow \qquad \Delta E = h\,C\,\bar{\partial}$$

Substituting $\bar{\partial}$ for its formulagives:

$$\boxed{\Delta E = h\,C\,R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

Example 5

Calculate the energy gapwhen an electron is removed from an H-atom in lyman series.



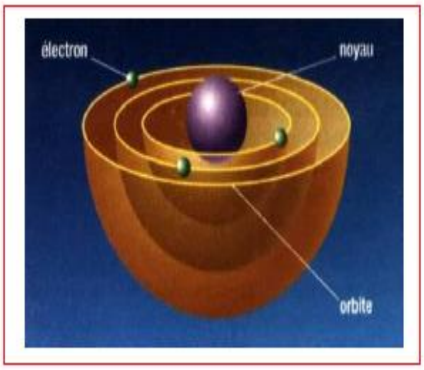
IV- Bohr’s atomic model: hydrogen atom

Bohr set down the following postulates to account for :

- The stability of the hydrogen atom (that the atom exists and its electron does not continuously radiate energyand spiral into the nucleus)
- The line spectrum of the atom.

1. Bohr’sPostulates

- Bohr proposed that in an atom electron is revolving around the nucleus in a definite circular path called **orbits**. These orbits are called ‘**stationary orbits**’ and each orbit or shell possesses fixed energy.
- Energy-level Postulate:An electron can have only *specific energy values in an atom*, which are called its energy levels. Therefore, the atom itself can have only specific total energy values. Thus, the electron in the lower energy state is called the **ground state**.



- The energy levels are represented by an integer called quantum numbers where n = 1, 2, 3…. These integers indicate **principal quantum numbers.**Various energy levels are designed as K(n=1), L(n=2), M(n=3) …. etc.
- The electron's angular momentum is quantized in its orbitals. So, electrons can move only those permissible orbits that should be an integral multiple of $\frac{h}{2\pi}$ where h is the Planck's constant. Thus, the Bohr's quantum condition wrote.

(Bohr's quantum condition)

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

Where, m = mass of the electron, r = radius of the electronic orbit, v = velocity of the electron in its orbit.

- Transitions Between Energy Levels:An electron in an atom can change energy only by going from one energy level to another. By so doing, the electron undergoes a ***transition***.

$$\boxed{\Delta E = E_{final} - E_{initial} = h\partial = hC\bar{\partial}}$$

- The electron gains energy when it jumps from a lower energy level to a higher energy level and the electron loses its energy as it jumps from the higher energy to a lower energy level.

2. Advantages of Bohr'stheory

Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen and H-like atomsand it gave the characteristics of electron in his orbit.

2.1- Calculation of energy of electron in Bohr's orbit

Bohr showed that the energies that an electron in hydrogen atom can occupy are given by :

Total Energy

$$\boxed{E_t = E_c + E_p}$$

PotentialEnergy

KineticEnergy

The force of attraction between the nucleus and the electron, **F_{ce}**,is equal to centrifugal force, **F_c**, of the moving electron:

$$|\vec{F_{Ce}}| = |\vec{F_c}| \begin{cases} \boxed{|\vec{F}_{ce}| = \dfrac{KZ|qq'|}{r^2}} \\ \\ \boxed{|\vec{F_c}| = \dfrac{m_e v^2}{r}} \end{cases}$$

$$\boxed{k = \frac{1}{4\pi\varepsilon_0} = \begin{cases} 9 \times 10^9 (MKSA) \\ 1\ (CGS) \end{cases}}$$

Where, q_1 and q_2 are the charges of nucleus and of electron, respectively. r is the distance between the nucleus and the electron. ε_0 is the permittivity constant: = $8.85 \times 10^{-12}\ C^2/(N \cdot m^2)$

For an electron:

$$|\vec{F_{Ce}}| = |\vec{F_c}| \quad \rightharpoonup \quad \frac{Ke^2}{r^2} = \frac{mv^2}{r} \quad \rightharpoonup \quad \boxed{mv^2 = \frac{Ke^2}{r}}$$

Since $E_C = \frac{1}{2} mv^2$ $\rightarrow$ $\boxed{E_c = \frac{1}{2}\frac{ke^2}{r}}$

In another side, the force acting on the electron is calculated as: $F_c = \frac{dE_p}{dr}$; where dE_p is the variation in the potential energy and $dr$is the variation in radius of the electronic orbit.

$$\int_0^{E_P} dE_p = \int_\infty^r F_c.dr = \int_\infty^r \frac{Ke^2}{r^2}\,dr \quad \Rightarrow \quad \boxed{E_p = -\frac{ke^2}{r}}$$

Substituting E_c and $E_p$for their formula in$E_t$gives:

$$\boxed{E_{t=} \frac{-KZe^2}{2r}}$$

2.2- Calculation of radius of Bohr's orbit

$$mv^2 = \frac{KZe^2}{r} \qquad\qquad m^2v^2 = \frac{mKZe^2}{r} \qquad (1)$$

And from Bohr's quantum condition, we write:

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

Substituting of *K*, gives us:

$$\boxed{r = \frac{h^2\varepsilon_0}{\pi m e^2}\frac{n^2}{Z}}$$

Where, *n* =Orbit number, *m* = 9.1×10^{-31}Kg, e =1.6 $\times10^{-19}$c, *Z* =Atomic number of element,ε_0 = 0.884×10^{-11} $c^2/N.m^2$, h=6.62×10^{-34}j.s.

After putting the values of *m*,*e*,ε_0,*h*, we get.

$$\boxed{r_n = a_0\frac{n^2}{Z}}$$

Thus, a_0 is the radius of the first orbit of hydrogen atom. Where

$$\boxed{a_0 = 0.53\ \text{Å}}$$

Substituting of r and kin the energy formula, gives us:

$$\boxed{E_{t=}\frac{-me^4Z^2}{8\varepsilon_0^2h^2n^2}}$$

In ground state energy of atom is minimum and for 1st orbit of H-atom, n=1.

$$\boxed{E_1=-13.54\ ev}$$

Putting the value of E_1,we get :

$$\boxed{E_n = E_1\frac{Z^2}{n^2}}$$

Exercise 6

1- The frequency of the shortest wavelength transition in Balmer series of atomic hydrogen is 8.227×10^{14} s^{-1}. Calculate R_H, the Rydberg constant.

2- Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

2.3- Calculation of velocity of electron

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

Substituting of r, gives us

$$v = \frac{h}{2\pi m a_0}\frac{Z}{n}$$

v_1 is the velocityof hydrogen atom:

$$V_1 = 2{,}18 \times 10^6 m/$$

Substituting of r, gives us:

$$V_n = V_1 \frac{Z}{n}$$

2.4- Ionizationenergy

Also called the **first ionization energy, E_i ,** is the energy required to remove an electron from **his stable orbit** to **the infinity ∞**.

$$E_i = E_\infty - E_n$$

$$E_n = E_1\frac{Z^2}{n^2} \quad \text{and} \quad E_\infty = 0 \quad \Rightarrow \quad E_i = -E_n = E_1\frac{Z^2}{n^2}$$

Exercise 7

- Light radiation of wavelength 10 nm (uv rays) can ionize a H-like atom in its ground state.
  1- Calculate the atomic number.
  2- What is the radius of the orbit in the 1st excited state of this atom ?
  3- Calculate the force of attraction between the nucleus and the electron in this orbit.
- Calculate the velocity of electron in the second Bohr orbit of excited state ofH atom. What is the wavelength associated to this electron ?

V- The hydrogen atom in wave mechanics

Bohr’s theory firmly established the concept of atomic energy levels. It was unsuccessful,however, in accounting for the details of atomic structure. Further understanding of atomic structurerequired other theoretical developments.

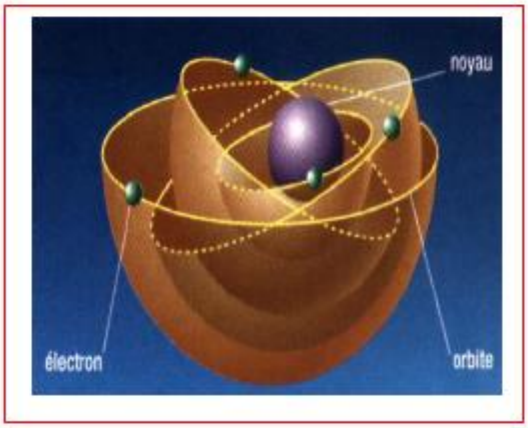
1- Limitations of Bohr’s Model of an Atom

- Bohr Theory could not explain the line spectra of atoms containing more than one electron.
- This theory could not explain the presence of multiple spectral lines.

- This theory could not explain the splitting of spectral lines in magnetic field (Zeeman Effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.
- This theory was unable to explain of dual nature of matter as explained on the basis of De broglies concept.
- This theory could not explain uncertainty principle.
- No conclusion was given for the concept of quantisation of energy.

2- Bohr – Sommerfeld's model

In **1915**, **ArnoldSommerfield** introduced a new atomic model to explain the fine spectrum of hydrogen atom. He gave concept that electron revolve round the nucleus in ***elliptical orbit***. Circular orbits are formed in special conditions only when major axis and minor axis of orbit are equal.

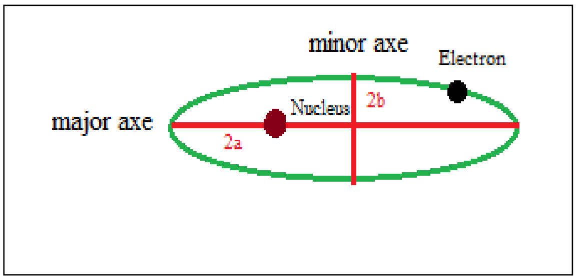


2.1. Azimuthal (Angular Momentum)

The azimuthal, or angular momentum, **ℓ**, defines the type or shape of the orbital where the electron most probably resides. It is the to be determined as its value relies only on n.

For circular orbit, the angular momentum=$\frac{nh}{2\pi}$where *n*= principal quantum number only one component. For elliptical orbit, another quantum number k, where the relation between n and k is :

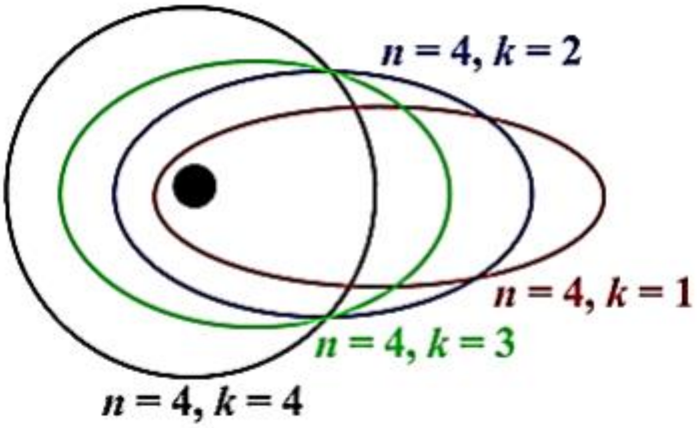
$$\boxed{e=\frac{b}{a}=\frac{k}{n}}$$

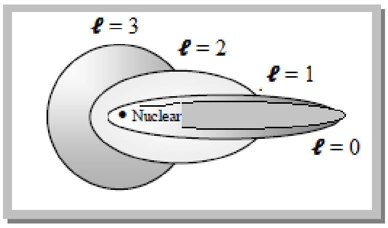


Thus Sommerfield showed that Bohr's each major level was composed of several sub-levels or subshells with a new **quantum number** **ℓ**called the **second quantum number**, where $\boxed{k = \ell + 1}$

Since $0 \le e \le 1 \Rightarrow 0 \le \frac{k}{n} \le 1 \Rightarrow 0 \le \frac{\ell+1}{n} \le 1$

So, $$\boxed{0 \le \ell \le n-1}$$





For, n = 4 ;**ℓ** = 0 ; **4s** sub shell e = 1/4 ellipse more flatter

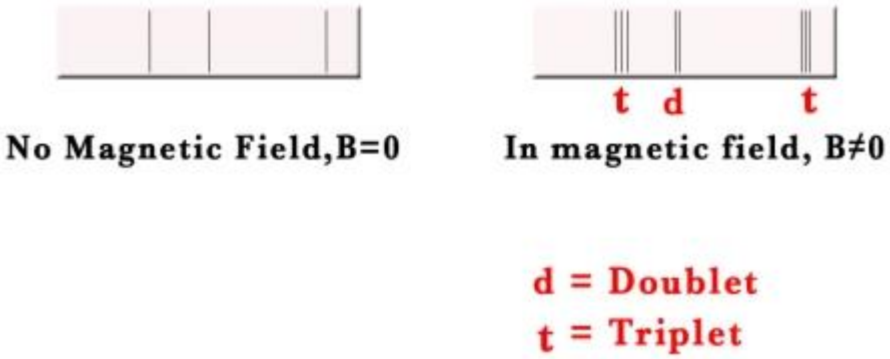
ℓ=1 ;**4p** sub shell e = 2/4 ellipse flatter

ℓ=2 ;**4d** sub shell e = 3/4 ellipse less flatter

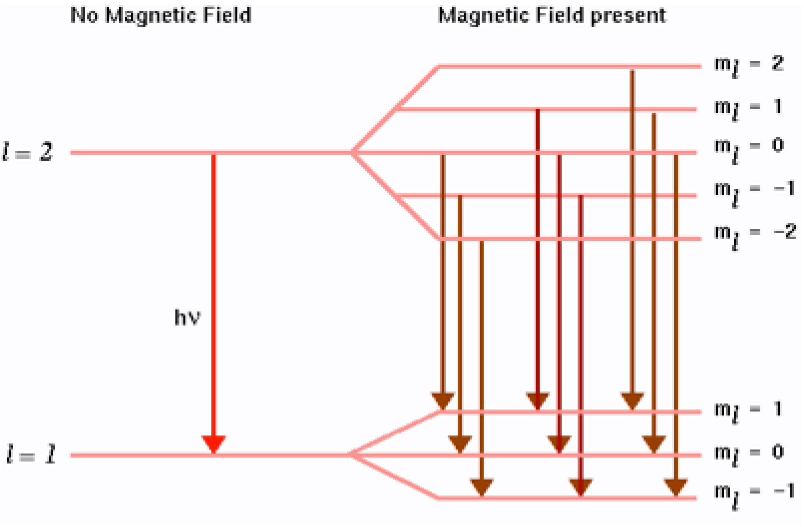
ℓ=3 ;**4f** sub shell e = 4/4circular

3- Magnetic quantum numbers m(Noble prize in 1902)

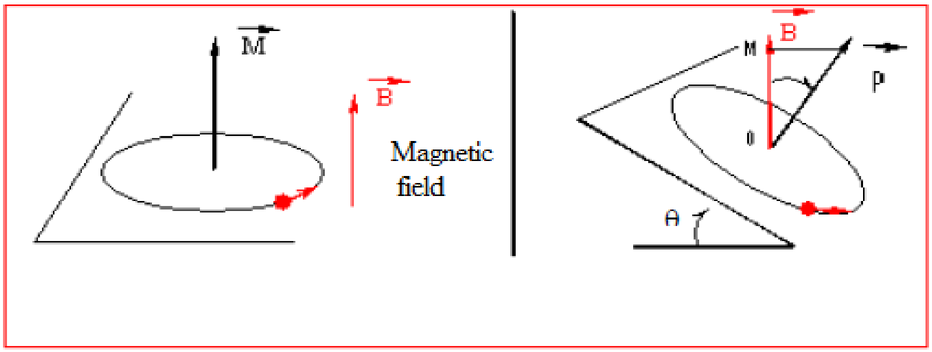
It was proposed by **Zeeman** and denoted by 'm'. It gives the number of permitted orientation of subshells. It tells about the splitting of spectral lines **into doublets or triplets**in the magnetic field i.e. this quantum number proved the Zeeman effect.



Degenerate orbitals : Orbitals having the same energy are known as degenerate orbitals.



The origin of Zeeman effect is the following. In an atomic energy state, an electron orbits around the nucleus of the atom and has a magnetic dipole moment $\|\overrightarrow{OM}\|$ associated with its angular momentum p. In a magnetic field, it acquires an additional energy just as a bar magnet does and consequently the original energy level is shifted. The energy shift may be positive, zero, or even negative, depending on the angle between the electron magnetic dipole moment and the field.

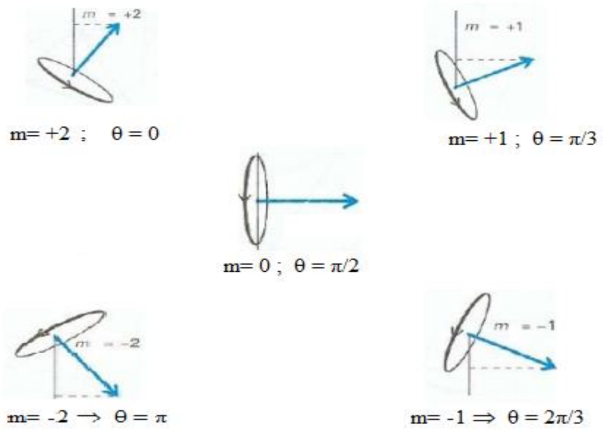


$$\boxed{\|\overrightarrow{OM}\| = p\cos\theta}$$

$$\|\overrightarrow{OM}\| = \frac{mh}{2\pi} \qquad \Rightarrow\Rightarrow \qquad \frac{mh}{2\pi} = p\cos\theta \qquad \frac{mh}{2\pi} = \frac{\ell h}{2\pi}\cos\theta$$

$$\boxed{\mathrm{Cos}\ \theta = \frac{m}{\ell}}$$

$-1 \leq \cos\theta \leq +1 \quad \Rightarrow \quad -1 \leq \frac{m}{\ell} \leq +1 \quad \Rightarrow \quad \boxed{-\ell \leq m \leq +\ell}$



m= +2 ; θ = 0

m= +1 ; θ = π/3

m= 0 ; θ = π/2

m= -2 → θ = π

m= -1 ⇒ θ = 2π/3

ℓ = 2 so -2 ≤ m ≤ +2 give m = -2, -1, 0, 1, 2

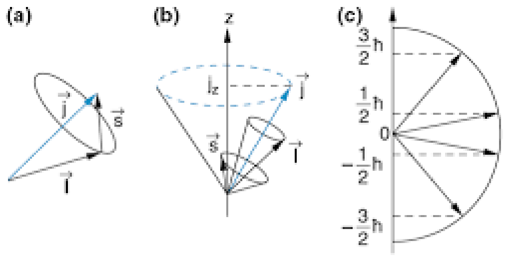


Fig.5.23 (a) Coupling of l and s and their precession around the space-fixed vector $j = l + s$ without external field. (b) Precession of j in an external magnetic field B_z. (c) Possible orientations of j with components $j_z = m\hbar$

4- The Spin Quantum Number(s)

In **1921**, **Otto Stern and Walter Gerlach**, conducted an experiment to study the magnetic properties of a single electron. They shot a beam of silver atoms through a slit and passed this beam through a non-uniform magnetic field. They choose Silver metal to conduct the experiment because it contains a single electron in its outermost shell 5S (ℓ =0, m =0),so technically it would not interact with any external magnetic field. Also, silver is easily detectable on a photographic plate. Instead, they saw that the field split the beam into two separate parts!

The only paussible reason for this observation was that the electron had two different orientations of the magnetic moment. Even after making these observations, Otto Stern and Walter Gerlach, could not conceive the idea of electron spins themselves. It was in **1925**, that **Samuel A. Goudsmit and George E. Uhlenbeck** conceptualized the idea of **electron spins**! They proposed that the electron doesn't just revolve around the nucleus but also spins around itself. This was the birth of the fourth quantum number :**the spin quantum number(s)** :

$$\boxed{S = \pm\frac{1}{2}}$$

5- Heisenberg's uncertainty principle

One of the important consequences of the dual nature of an electron is the uncertainty principle, developed by ***Warner Heisenberg***.

According to uncertainty principle "It is impossible to specify at any given moment both the position and momentum (velocity) of an electron".Mathematically it is represented as,

$$\boxed{\Delta Q\ .\Delta x\ \geq h}$$

Where,Δx is uncertainty position of the particle, Δp= mΔv uncertainty in the momentum of the particle.

So equation becomes, $\Delta x\ .m\ \Delta v \geq \frac{h}{4\pi}$ or $\Delta x\ .\Delta v \geq \frac{h}{4\pi m}$

The sign≥ means that the product ofΔx andΔp (or of Δx and Δv) can be greater than, or equal to but never smaller than $\frac{h}{4\pi m}$.If Δx is made small,Δp increases and vice versa.

In terms of uncertainty in energy, ΔEand uncertainty in time Δt, this principle is written as :

$$\Delta E\ .\Delta t \geq \frac{h}{4\pi}$$

Heisenberg's uncertainty principle cannot apply to a stationary electron because its velocity is 0 and position can be measured accurately.

Exercise 8

a- Calculate the uncertainty (in meters) in the position of a 120 g baseball thrown at a velocity of 45 m/s if the uncertainty in the velocity is 2%.

b- The mass *m* of an electron is 9.11×10^{-31} kgand the velocity *v* of an electron in a hydrogen atom is 2.2×10^{6} m/s. If we assume that the velocity is known to within 10%, or 0.2×10^{6}m/s. calculate the uncertainty in the electron's position in a hydrogen atom.

VI-Poly electronic atoms in wave mechanics

Bohr made a significant contribution to our understanding of atoms. But his theory did not provide a complete description of electronic behavior in atoms and this approach could not account for the emission spectra of atoms containing morethan one electron, such as atoms of helium and lithium.

In **1926** the Austrian physicist **Erwin Schrödinger**, using a complicated mathematical technique, formulated an equation that describes the behaviorand energies of submicroscopic particles in general. It is important to know, however,that the equation incorporates both particle behavior, in terms of mass *m*, and wavebehavior, in terms of a ***wave function***Ψ.

- Ψdepends on the location in space of the system which has no direct physical meaning.
- The **probabilityof finding**the electron in a certain region in space is proportional to the square ofthe wave function, Ψ^2.
- According to wave theory, the intensity of light is proportional to theΨ^2.
- The most likely place to find an electron iswhere the intensity is greatest, that is, where the value of Ψ^2 is greatest.
- A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron.

Orbit and orbital are not synonymous :

- An orbit, as proposed by Bohr, is a circular path around thenucleus in which an electron moves. A precise description of this path of the electron is impossibleaccording to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning andtheir existence can never be demonstrated experimentally.
- An atomic orbital, on the other hand,is a quantum mechanical concept and refers to the one electron wave function ψin an atom. It ischaracterized by three quantum numbers (*n*, *l* and *m*) and its value depends upon the coordinatesof the electron.

1- Klechkowski rules (Aufbau principle)

The filling of energy levels and sub-levels is produced in accordance with **Vsevolod. M. Klechkowski**rules which are based on the two solutions of the E. Schroedinger equation the principal n and the orbital ℓ quantum numbers.

- Each orbital in an atom is specified by a set of three quantum numbers (*n*, ℓ, *m*) and each electron is designated by a set of four quantum numbers (*n*, *l*, *m* and *s*).
- The maximum number of an electron in an orbit is $2n^2$
- The maximum number of electrons in subshell = $2(2\ell+1)$

S -subshell →2 electrons

p -subshell →6 electrons

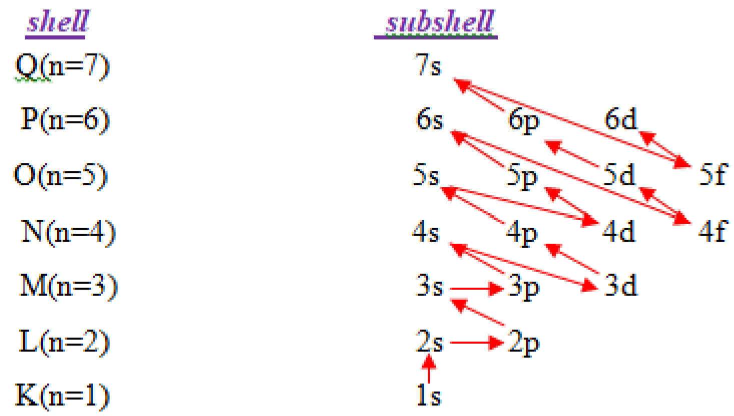
d -subshell →10 electrons

f -subshell →14 electrons

- The energy of any electron is depending on the value of ***n*** and **ℓ** because total energy = **(*n* + ℓ)**. The electron enters in that sub orbit whose (n + ℓ) value or the value of energy is less.
- For subshells with the same value of (n + ℓ), electrons are assigned first to the subshell with lower *n*.

$0 \le \ell \le n-1$

n	***ℓ***	**n+*ℓ***	Subshell
1	0	1	1S
2	0	2	2S
2	1	3	2P
3	0		3S
3	1	4	3P
4	0		4S
3	2	5	3d
4	1		4P
5	0		5S
4	2	6	4d
5	1		5P
6	0		6S
4	3	7	4f
5	2		5d
6	1		6P
7	0		7S

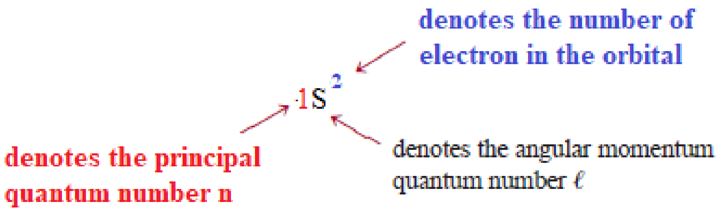


Exercise 9

Use quantum numbers to compare the energies of: 3s 3p 3d 4s 4p 4d 5s

1- Electron Configuration

The electron configuration of the atomis how the electrons are distributedamong the variousatomicorbitals, in order to understandelectronicbehavior.Recallthat the number of electrons in an atomisequal to itsatomicnumber Z.



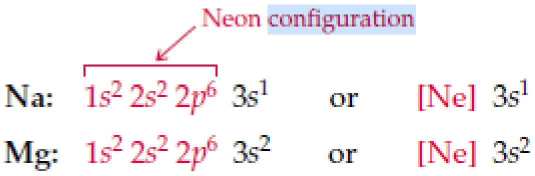
Twogeneralrules help us to predictelectron configurations :

- Electrons are assigned to orbitals in order of increasing value of (n + ℓ).
- For subshellswith the same value of (n + ℓ), electrons are assigned first to the subshellwithlower$n$.

Exemple: **$_8$O:** $1s^2\ 2s^2\ 2p^4$

Notethatweoftenwrite the configurations in a **shorthand version**by giving the symbol of the **noble gas**in the previousrow to indicateelectrons in filledshells and thenspecifyingonlythoseelectrons in unfilledshells.

Exemple :



Na: $\underbrace{1s^2\ 2s^2\ 2p^6}\ 3s^1$ or [Ne] $3s^1$

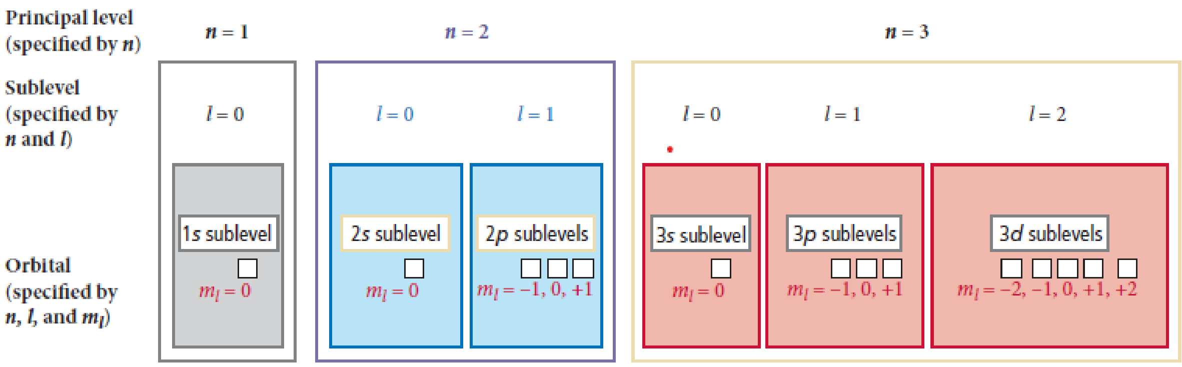
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ or [Ne] $3s^2$

Noble gas, isextremely stable and no reactions of it are known.Noble gaz are : **Helium ($_2$He), neon ($_{10}$Ne), argon ($_{18}$Ar), krypton ($_{36}$Kr), xenon ($_{54}$Xe), and radon ($_{86}$Rn).**

2- The AtomOrbitalsdiagram

The atomic orbital is representing with **a quantum box**. Electron in an orbital is shown by **an arrow**. The arrow points up when$S$=+½ and down when$S$ = -½ .Each quantum box holds a maximum of twice as many electrons as the number of orbitals in the subshell.

The following diagram shows all of the orbitals, each represented by a small square, in the first three principal levels.



3- The Pauli exclusion principle

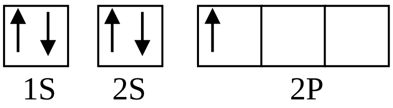
Wolfgang Pauli, Nobel Prize **1945**, states that *no twoelectrons in the same atom can have identical values for all four of their quantum numbers*.What this means is that no more than **two** electrons can occupy the same orbital, and that twoelectrons in the same orbital must have **opposite spins**.

If one electron in an atom has the quantum numbers $n = 1$, $l = 0$, $m = 0$, and $S = +1/2$, no other electron can have these same quantum numbers.

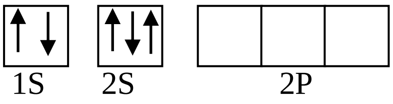
Exemple10

- Write down both the full electronic configuration and the noble gas notation of Br. Draw the electronic configuration of Br and C in box notation.
- Which of the following orbital diagrams or electron configurations are possible and which are impossible, according to the Pauli exclusion principle? Explain.

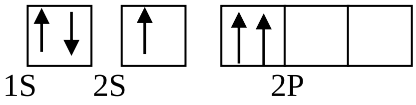
e-



f-



g-



4- Hund’sRule

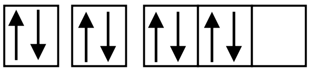
In about 1927, **Friedrich Hund** discovered an empirical rule determining the lowest energy arrangement of electrons in a subshell. Hund’s rule states that :

The lowest-energy arrangement of electrons in a subshell is obtained by putting electrons into separate orbitals of the subshell with the same spin before pairing electrons.

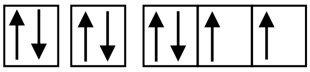
Exemple 11

1- Which of the following arrangements of electrons are possible and whichare impossible ?

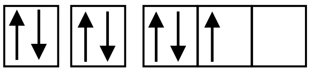
a-



b-



c-



2- Whatis the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

5- Electron Configurations of Ions

We have seen that ions are formed when atoms **gain or lose electrons**.

A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed.

An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 12 : Predicting Electron Configurations of Ion

Whatis the electron configuration and orbital diagram of:

a. Na$^+$
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

First, write out the electron configuration and formation for each parent atom. Next, determinewhether an electronisgained or lost. Rememberelectrons are negativelycharged, so ions witha positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electronbefore the *d* orbitals.

CHAPTER 5.

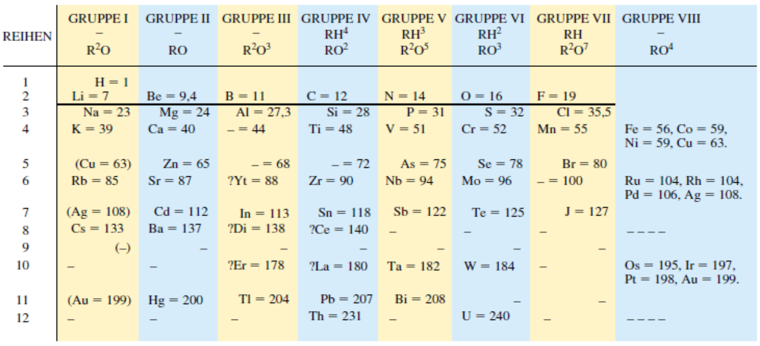
PERIODIC CLASSIFICATION OF ELEMENTS

Chapter contents

- **Periodic classification of D. Mendeleev,**
- **Modern periodic classification,**
- **Evolution and periodicity of the physico-chemical properties of the elements,**
- **Calculation of radii (atomic and ionic),**
- **The successive ionization energies,**
- **Electron affinity and electronegativity (Mulliken scale) by Slater's rules**

I- Periodic classification of D. Mendeleev

In 1869 the Russian chemist **Dmitri Ivanovich Mendeleev** (1834–1907) and the German chemist **J. Lothar Meyer** (1830–1895), working independently, made similar discoveries. They found that when they arranged the elements in order of atomic mass, they could place them in horizontal rows, one row under the other, so that the elements in each vertical column have similar properties. A tabular arrangement of elements in rows and columns, highlighting the regular repetition of properties of the elements, is called a **periodic table.**



REIHEN	GRUPPE I – R^2O	GRUPPE II – RO	GRUPPE III – R^2O^3	GRUPPE IV RH^4 RO^2	GRUPPE V RH^3 R^2O^5	GRUPPE VI RH^2 RO^3	GRUPPE VII RH R^2O^7	GRUPPE VIII – RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	– = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	– = 68	– = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	– = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	–	–	–	– – – –
9	(–)	–	–	–	–	–	–	
10	–	–	?Er = 178	?La = 180	Ta = 182	W = 184	–	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	–	–	
12	–	–	–	Th = 231	–	U = 240	–	– – – –

Figure 4-1 Mendeleev's early periodic table (1872). "J" is the German symbol for iodine.

II- Modern periodic classification

In the early part of this century, it was shown that the elements are characterized by their atomic numbers, rather than atomic masses. Each entry lists the atomic number, atomic symbol, and atomic mass of an element.

- This classification is called **periodic table** due to the repetition of similar outer shell electronic configuration at a certain regular intervals.

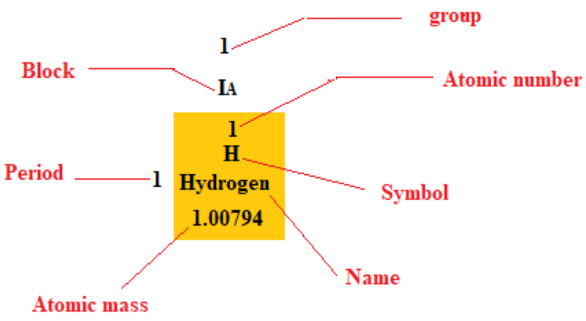
- It consists of 18 vertical columns called **groups**and 7 horizontal rows called **periods**.

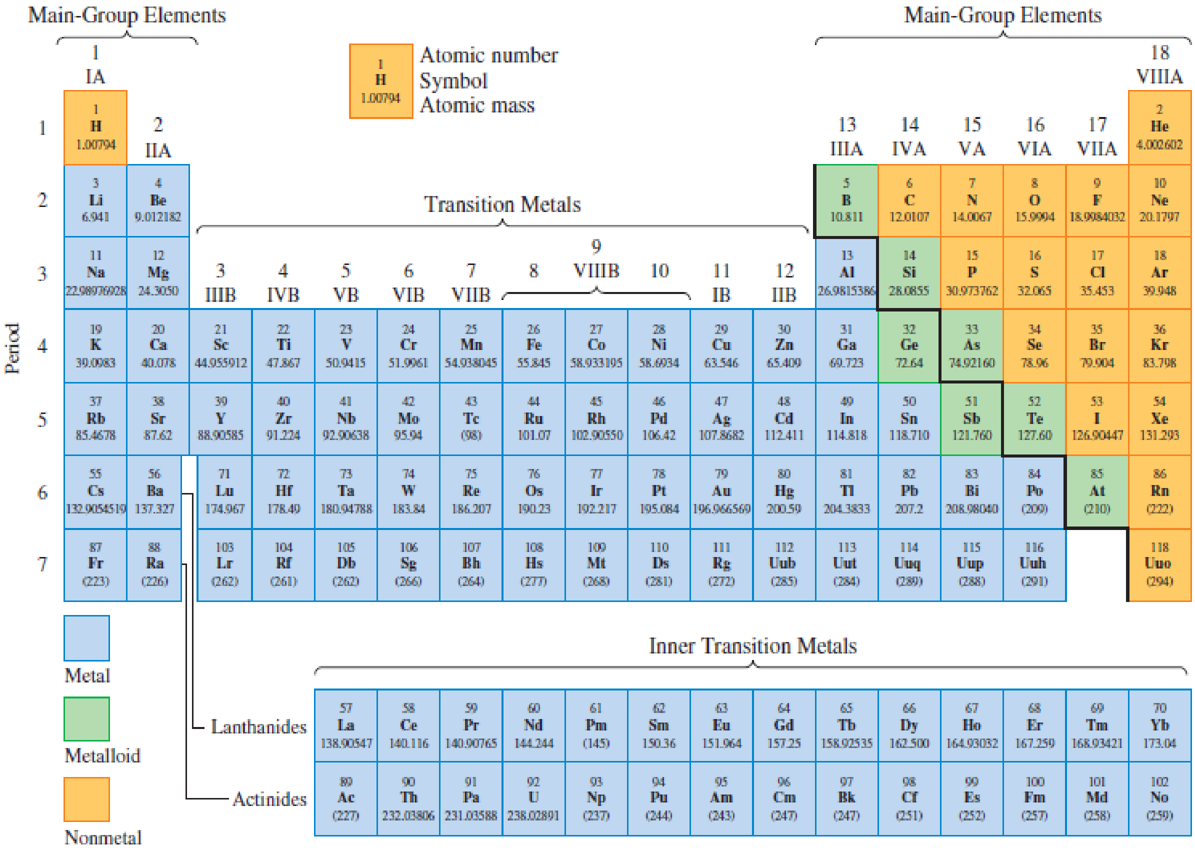
- At present, 118 elements are known to us. All these have different properties. Out of these 118, only 98 are naturally occurring.

1. Structural features of the periodic table

The basic structure of the periodic table is its division into rows (periods) and columns (groups). The elements in any one group have **similar properties** such as : radii, ionic radii, inert gas radii, Ionization enthalpy, electron gain enthalpy, electronegativity, valency.

For simplicity, chemists refer to specific elements using one- or two-letter symbols. The first letter of an element's symbolis always capitalized, and the second letter, if any, is lowercase. Many of the symbolsare just the first one or two letters of the element's English name. Other symbols derivefrom Latin or other languages: Na = sodium (Latin, *natrium*), Pb = lead (Latin, *plumbum*), W = tungsten (German, *wolfram*).





1 **H** 1.00794	Atomic number Symbol Atomic mass

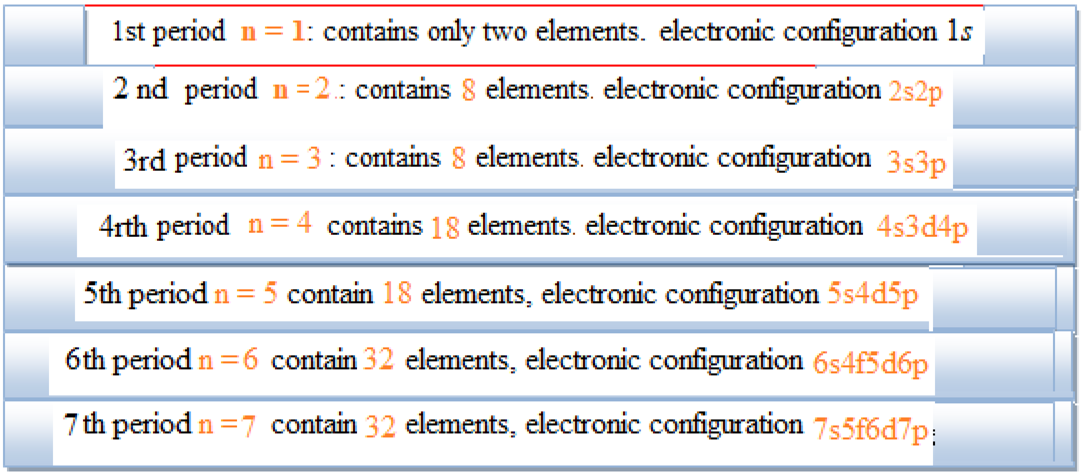
Period	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 **H** 1.00794																	2 **He** 4.002602
2	3 **Li** 6.941	4 **Be** 9.012182											5 **B** 10.811	6 **C** 12.0107	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984032	10 **Ne** 20.1797
3	11 **Na** 22.98976928	12 **Mg** 24.3050											13 **Al** 26.9815386	14 **Si** 28.0855	15 **P** 30.973762	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.955912	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.938045	26 **Fe** 55.845	27 **Co** 58.933195	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.409	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.92160	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.90585	40 **Zr** 91.224	41 **Nb** 92.90638	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.90550	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.90447	54 **Xe** 131.293
6	55 **Cs** 132.9054519	56 **Ba** 137.327	71 **Lu** 174.967	72 **Hf** 178.49	73 **Ta** 180.94788	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.966569	80 **Hg** 200.59	81 **Tl** 204.3833	82 **Pb** 207.2	83 **Bi** 208.98040	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	103 **Lr** (262)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 **Uub** (285)	113 **Uut** (284)	114 **Uuq** (289)	115 **Uup** (288)	116 **Uuh** (291)		118 **Uuo** (294)

Lanthanides	57 **La** 138.90547	58 **Ce** 140.116	59 **Pr** 140.90765	60 **Nd** 144.244	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.92535	66 **Dy** 162.500	67 **Ho** 164.93032	68 **Er** 167.259	69 **Tm** 168.93421	70 **Yb** 173.04
Actinides	89 **Ac** (227)	90 **Th** 232.03806	91 **Pa** 231.03588	92 **U** 238.02891	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)

1.1. Periods and Groups

➢ **A period :** consists of the elements in any one horizontal row of the periodic table.

✓ Element 118, the final element in the Periodic Table series, is **Oganesson**. Oganesson was discovered in 2002 and its properties defy our expectations based on trends in the periodic table.



1st period n = 1: contains only two elements. electronic configuration 1s

2 nd period n = 2 : contains 8 elements. electronic configuration 2s2p

3rd period n = 3 : contains 8 elements. electronic configuration 3s3p

4rth period n = 4 contains 18 elements. electronic configuration 4s3d4p

5th period n = 5 contain 18 elements, electronic configuration 5s4d5p

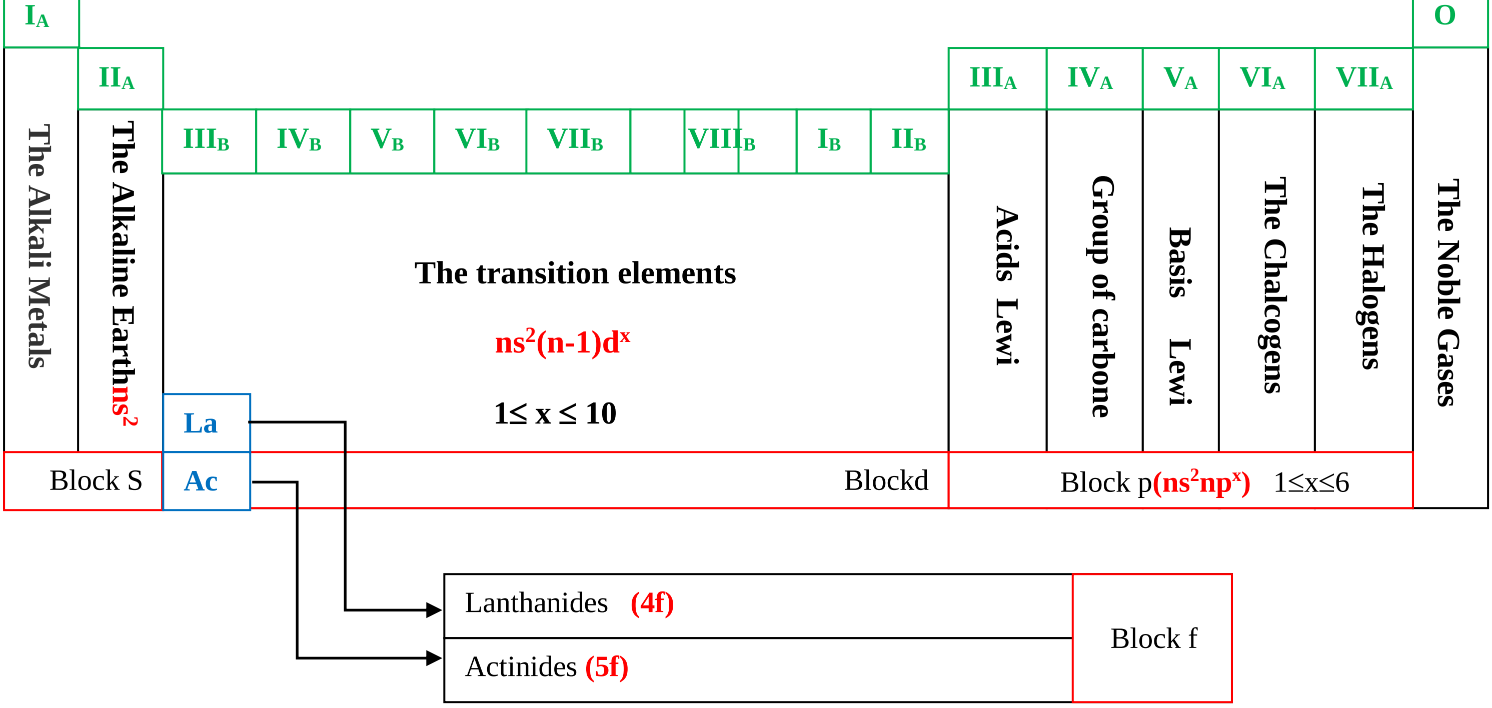
6th period n = 6 contain 32 elements, electronic configuration 6s4f5d6p

7 th period n = 7 contain 32 elements, electronic configuration 7s5f6d7p;

- ✓ The periodic table is complete in its neatest form – all seven periods of elements currently known are filled.
- ✓ The 14 elements with atomic numbers (Z) = 58 – 71 (occurring after lanthanum La in the periodic table) are called **lanthanides**or **rare earth elements**andare placed at the bottom of the periodic table. The valence electrons of these elements lie in the **4f** orbital.
- ✓ The 14 elements with atomic numbers (Z) = 90 – 103 (Occurring after actinium Ac in the periodic table) are called **Actinides**and are placed at the bottom of the periodic table. The valence electrons of these elements lie in the **5f** orbital.

➢ **Agroup**consists of the elements in any one column of the periodic table.

✓Groups 1, 2, and 13–18 are **the main group elements**, listed as ***A***in older tables. Groups 3–12 are in the middle of the periodic table and are **the transition elements**, listed as ***B***in older tables.

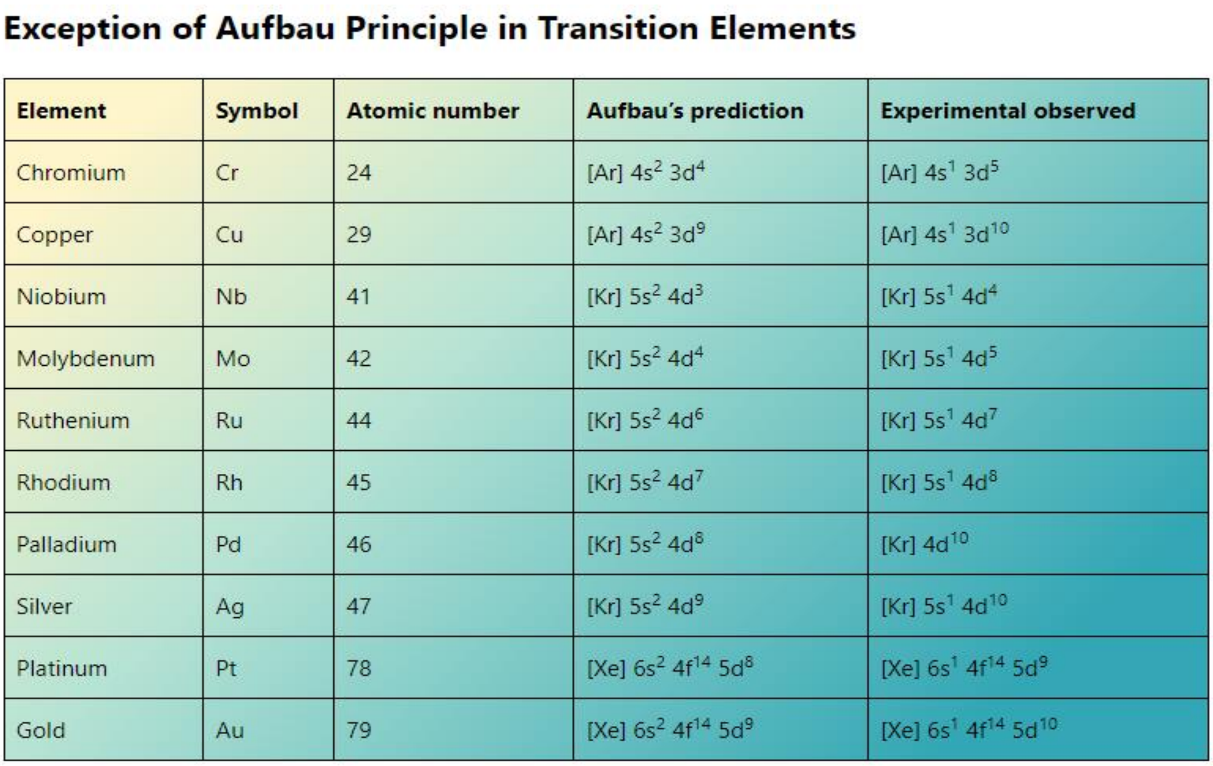


- ✓ **Group IA** are the **alkali metals**: These are (except for hydrogen) soft, shiny, low-melting, highly reactive metals, which tarnish when exposed to air. The valence electron is easily lost, forming an ion with a 1+ charge.
- ✓ **Group IIA** are the **alkaline earth metals :** In most cases, the alkaline earth metals are ionized to form a 2+ charge.
- ✓ There are exceptions of Aufbau Principle in transition elements where, one electron has passed from the s-orbital to a d-orbital to generate a half-filled or filled subshell. In this case, the usual explanation is that "half-filled or completely filled subshells are particularly stable arrangements of electrons". However this is not supported by the facts, as tungsten (W) has a Madelung-following $d^4\ s^2$ configuration and not $d^5\ s^1$, and niobium (Nb) has an anomalous $d^4\ s^1$ configuration that does not give it a half-filled or completely filled subshell.

Exemples :

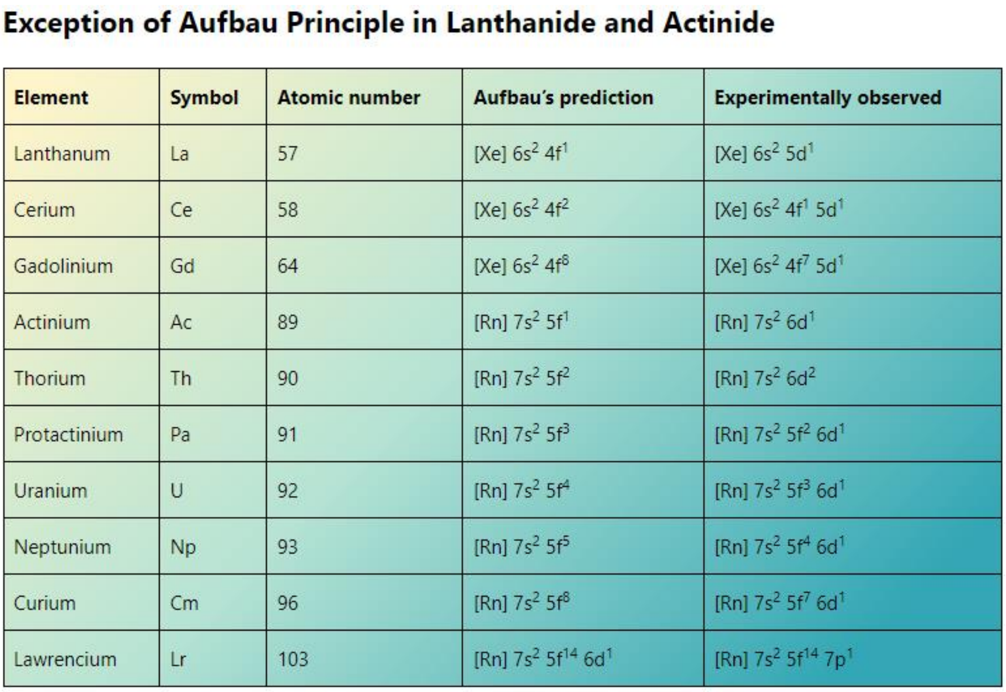
Rather than $_{24}Cr : 1s^22s^22p^63s^23p^64s^23d^4$, Cr's electronic configuration is $_{24}Cr : 1s^22s^22p^63s^23p^6\underline{4s^13d^5}$

Rather than $_{64}Gd : 1s^22s^22p^63s^23p^64s^23d^{10}4p^6\ 5s^24d^{10}5p^66s^24f^8$, Gd's E.C is $_{64}Gd$: $1s^22s^22p^63s^23p^64s^23d^{10}4p^6\ 5s^24d^{10}5p^66s^2\underline{4f^75d^1}$



Exception of Aufbau Principle in Transition Elements

Element	Symbol	Atomic number	Aufbau's prediction	Experimental observed
Chromium	Cr	24	[Ar] $4s^2\ 3d^4$	[Ar] $4s^1\ 3d^5$
Copper	Cu	29	[Ar] $4s^2\ 3d^9$	[Ar] $4s^1\ 3d^{10}$
Niobium	Nb	41	[Kr] $5s^2\ 4d^3$	[Kr] $5s^1\ 4d^4$
Molybdenum	Mo	42	[Kr] $5s^2\ 4d^4$	[Kr] $5s^1\ 4d^5$
Ruthenium	Ru	44	[Kr] $5s^2\ 4d^6$	[Kr] $5s^1\ 4d^7$
Rhodium	Rh	45	[Kr] $5s^2\ 4d^7$	[Kr] $5s^1\ 4d^8$
Palladium	Pd	46	[Kr] $5s^2\ 4d^8$	[Kr] $4d^{10}$
Silver	Ag	47	[Kr] $5s^2\ 4d^9$	[Kr] $5s^1\ 4d^{10}$
Platinum	Pt	78	[Xe] $6s^2\ 4f^{14}\ 5d^8$	[Xe] $6s^1\ 4f^{14}\ 5d^9$
Gold	Au	79	[Xe] $6s^2\ 4f^{14}\ 5d^9$	[Xe] $6s^1\ 4f^{14}\ 5d^{10}$



Exception of Aufbau Principle in Lanthanide and Actinide

Element	Symbol	Atomic number	Aufbau's prediction	Experimentally observed
Lanthanum	La	57	$[Xe]\ 6s^2\ 4f^1$	$[Xe]\ 6s^2\ 5d^1$
Cerium	Ce	58	$[Xe]\ 6s^2\ 4f^2$	$[Xe]\ 6s^2\ 4f^1\ 5d^1$
Gadolinium	Gd	64	$[Xe]\ 6s^2\ 4f^8$	$[Xe]\ 6s^2\ 4f^7\ 5d^1$
Actinium	Ac	89	$[Rn]\ 7s^2\ 5f^1$	$[Rn]\ 7s^2\ 6d^1$
Thorium	Th	90	$[Rn]\ 7s^2\ 5f^2$	$[Rn]\ 7s^2\ 6d^2$
Protactinium	Pa	91	$[Rn]\ 7s^2\ 5f^3$	$[Rn]\ 7s^2\ 5f^2\ 6d^1$
Uranium	U	92	$[Rn]\ 7s^2\ 5f^4$	$[Rn]\ 7s^2\ 5f^3\ 6d^1$
Neptunium	Np	93	$[Rn]\ 7s^2\ 5f^5$	$[Rn]\ 7s^2\ 5f^4\ 6d^1$
Curium	Cm	96	$[Rn]\ 7s^2\ 5f^8$	$[Rn]\ 7s^2\ 5f^7\ 6d^1$
Lawrencium	Lr	103	$[Rn]\ 7s^2\ 5f^{14}\ 6d^1$	$[Rn]\ 7s^2\ 5f^{14}\ 7p^1$

- ✓ **Group VIIIB**is called Triad. It is composed of elements which share similar chemical and physical characteristics. They are found adjacent to each other in period 4 of the periodic table.

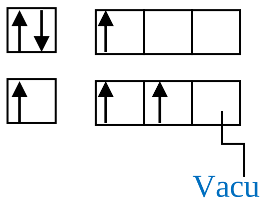
Fe	Co	Ni
Ra	Rh	Pd
Os	Ir	Pt
$ns^2(n-1)d^6$	$ns^2(n-1)d^7$	$ns^2(n-1)d^8$

- ✓ **Group IIIA** is called**Lewis Acids**, which are electron pair ***acceptors***.

Exemple:

$_5B : 1s^22s^22p^1$

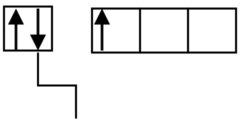
$_5B :_2[He]\ 2s^22p^1$



- ✓ **Group VA** is called**BasesAcids**, which are electron pair ***donors***.

Exemple : $_7N : 1s^22s^22p^3$

$_7N :_2[He]\ 2s^22p^3$



- ✓ **Group VIIA**is called**The Halogens:** include fluorine, chlorine, bromine, and iodine. Astatine is also in the group, but is radioactive and will not be considered here. They are strong oxidizing agents and are readily reduced to the X^- ions, and so the halogens form numerous ionic compounds.

- ✓ **Group O is the Noble Gases :** are the naturally occurring members of column 18 ofthe periodictable: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe),andradon(Rn). All the orbitals in the valence shell of the noble gasesare completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons.

1.2. Classification in Blocks

In yet another classification, the long form of the periodic table has been divided into four blocks (i.e. s, p, d and f), depending upon the subshell to which the last electron enters.

- **s-block elements :**The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the *s*-Block Elements.

- **p-block elements :**The ***p*-Block Elements** comprise those belonging to Group 13 to 18 and these together with the *s*-Block Elementsare called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6in each period. At the end of each period isa noble gas element.

- **d-block elements:**These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner *d* orbitals by electrons and are therefore referred to as *d*-Block Elements. These elements have the general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$.

- **f-block elements :**The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids,Ce(Z = 58) – Lu(Z = 71) and Actinoids, Th(Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n-2)f^{1-14}$ $(n-1)d^{0-1}ns^2$. The last electron added to each element is filled in *f*- orbital.

2. Position of Elements in the Periodic Table

2.1. Outermost shells : The outermost shell is known as the valence shell, and the electrons found in it are called valence electrons. If the outer shell of an atom has less than its maximum number of electrons then it will not be stable. It will react with other atoms to get a full outer shell.

2.2. Inner shellelectrons are any electrons not in the outermost shell and they are the core electrons.

2.3. Valency : The valency of an element is determined by the number of valence electrons present in the outermost shell of its atom. It determine the kind and number of bonds formed by an element.

$$\overset{\text{Valency = 8}}{} \quad {}_{26}\text{Fe} : {}_{18}\underbrace{[\text{Ar}]}_{\text{Inner shell}}\underbrace{4s^2 3d^6}_{\text{Outermost shell}}$$

Valence is the number of electrons an atom must lose or gain to attain the nearest noble gas or inert gas electronic configuration. **“Electrons in the outer shells that are not filled ”**.

Since **filled *d* or *f*** subshells are seldom disturbed in a chemical reaction, we can define valence electrons as follows: **The electrons on an atom that are not present in the previous rare gas, ignoring filled d or f subshells**.

Exemple

Gallium therefore has three valence electrons.

${}_{31}\text{Ga} : {}_{18}[\text{Ar}]\ 4s^2 3d^{10} 4p^1$

The **shorthand version** of gallium is

$${}_{31}\text{Ga} : {}_{18}\underbrace{[\text{Ar}]3d^{10}}_{\text{the core electrons = 28}}\ \underbrace{4s^2 4p^1}_{\text{valence electrons= 3 (outermost shell)}}$$

Exercise 1

- What neutral elements have each electron configuration below?

- $1s^2\ 2s^2\ 2p^3$
- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
- $[\text{Ne}]\ 3s^2\ 3p^3$
- $[\text{Kr}]\ 5s^2\ 4d^5$

- How many core and valence electrons are in each atom above?

❖ Electron Configurations and the Periodic Table

- The subshell, to which the last electron enters in the electronic distribution, defines the block of the element.

- An element belongs to **A liste** if the subshellthat receives the last electron in the electron configuration is **p or s**.

- An element belongs to **B liste** if the subshell that receives the last electron in the electron configuration is **d or f**.

Exemple : oxygen electronic configuration is : $_8O$: $1s^2 2s^2 2p^4$

The last electron enters in the subshell p, so oxygen belongs to p-block and group **A**.

- The group of an element is determined by the number of valence electrons.
- The period corresponds to the largest principal quantum number n in the electron configuration.
- The column represents the total number of electrons that come after the noble gas.

Exemple :

- $_{12}Mg$: $1s^2 2s^2 2p^6 3s^2$:$_{10}[Ne]3s^2$ valency = 2

The largest principal quantum number n = 3

The last electron enters in the subshell s (liste A)

so Mg belongs to s-block and group II_A and 3rd period and column 2.

- $_{29}Cu$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$: $_{18}[Ar]3d^{10}\,4s^1$ valency = 1

The largest principal quantum number n = 4

The last electron enters in the subshell d (liste B)

so Cu belongs to d-block and group I_B and 4th period and column 11.

- $_{40}Zr$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6\, 5s^2 4d^2$
- : $_{36}[Kr]5s^2 4d^2$ valency = 4

The largest principal quantum number n = 5

The last electron enters in the subshell d (liste B) so Zr belongs to d-block and group IV$_B$ and 5th period and column 4.

Exercise 2

- What is the position of the element in the periodic table satisfying the electronic configuration $(n-1)d^1ns^2$ for n=4?
- Germanium Ge belongs to the column of${}_6$C and the period of${}_1$9K. Determine :
  1. Its position in the periodic table.
  2. Its atomic number.
  3. Describe the valence shell (number of electron pairs, single electrons and empty quantum box).
  4. Determine the four quantum numbers of the valence electrons.

Exercise 3

An element has fewer than 18 electrons and has two free electrons.

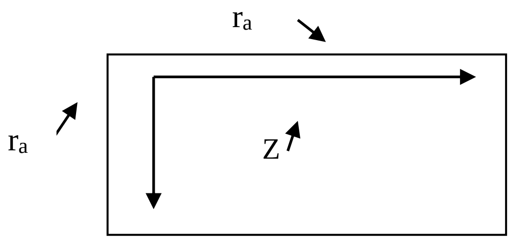
- What are the possible electronic distributions?
- What is the formula of this element, knowing that it belongs to the ${}_{50}$Sn’sgroup and the ${}_3$Li’speriod?

III- Evolution and periodicity of the physico-chemical properties of the elements

The position of an element in the Periodic Table tells us about itschemical reactivity.

IV- Calculation of radii (atomic and ionic)

- Atomic radius decreases from left to right across a period due to increasing Zbecause of the nucleus charge increases as Z increase.
- Atomic radius increases down a column of the periodic table because the distance of the electron from the nucleus increases as n increases.

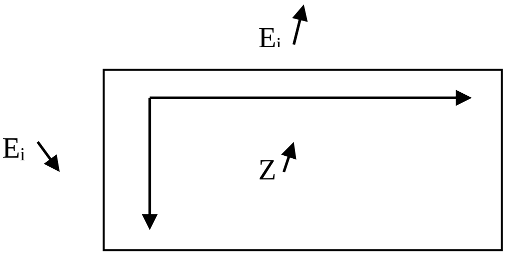


V-The successive ionization energie

Ionization energy (IE): minimum energy needed to remove an electron from an atom in the gas phase. In general, ionization energy increases as Z increases.

$$A \longrightarrow A^+ + 1e$$

- IE_i increases from left to right across a period due to increasing Z.
- IE_i decreases down a column of the periodic table because the distance of the electron from the nucleus increases as n increases.

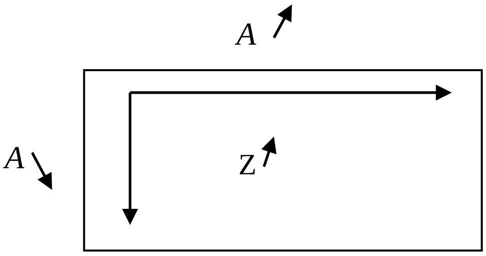


VI- Electron affinity and electronegativity (Mulliken scale) by Slater's rules

Electron Affinity (A): energy released when an atom in the gas phase accepts an electron.

$$X + 1e \longrightarrow X^- + A$$

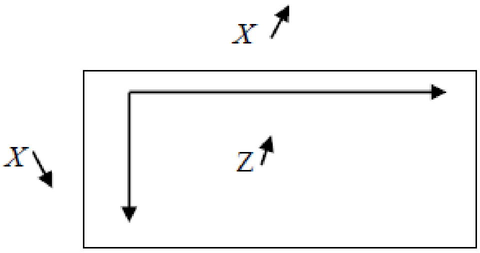
- A increases from left to right across a period due to increasing Z.
- A decreases down a column of the periodic table because the distance of the electron from the nucleus increases as n increases.



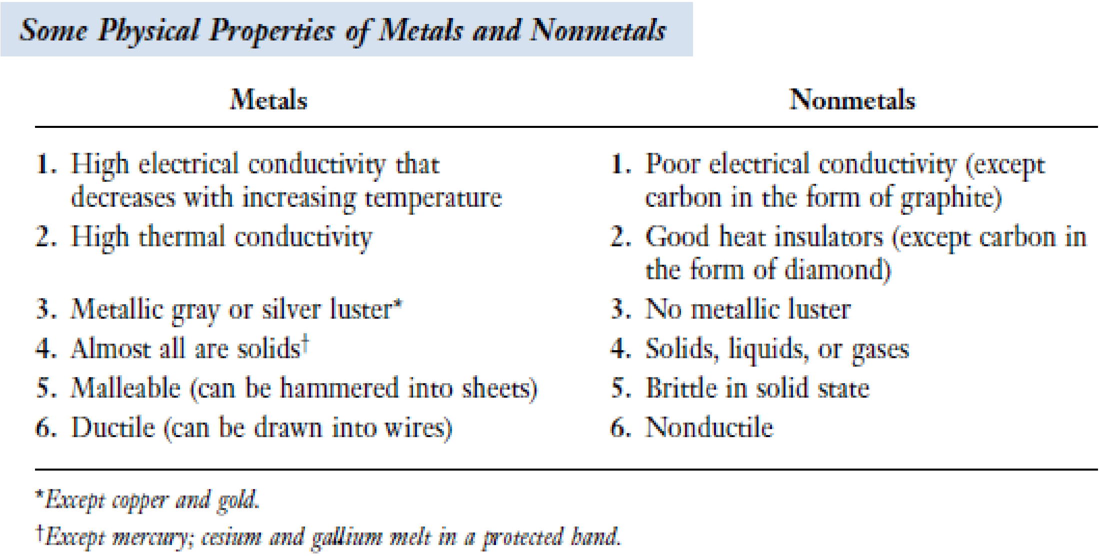
Electronegativity

A chemical property that describes the tendency of an atom or a functional group to attract electrons toward itself.

- χ increases from left to right across a period due to increasing Z.
- χ decreases down a column of the periodic table.



VII- Metals and Nonmetals

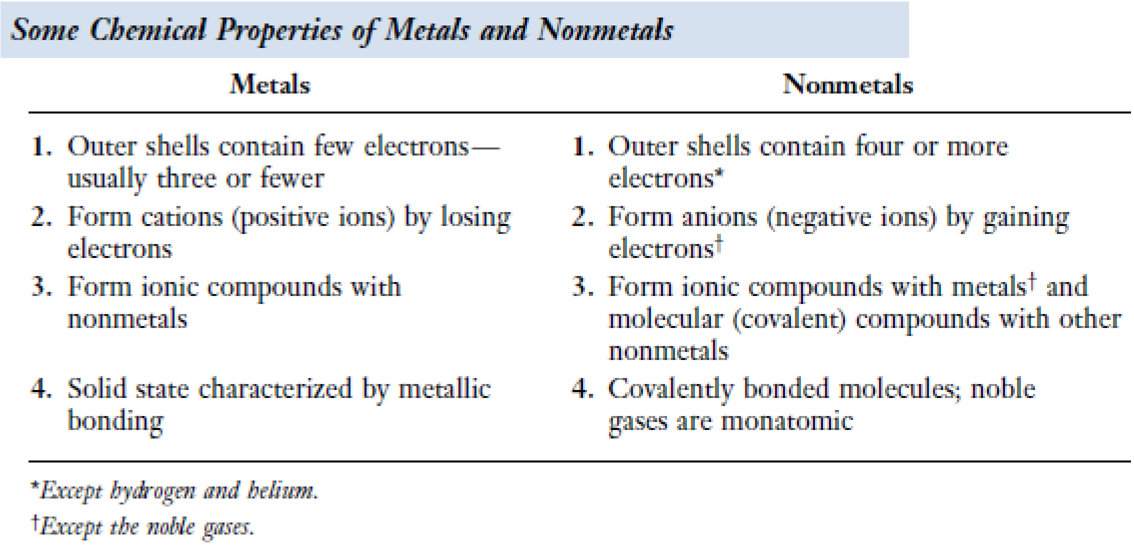


Some Physical Properties of Metals and Nonmetals

Metals	Nonmetals
1. High electrical conductivity that decreases with increasing temperature	1. Poor electrical conductivity (except carbon in the form of graphite)
2. High thermal conductivity	2. Good heat insulators (except carbon in the form of diamond)
3. Metallic gray or silver luster*	3. No metallic luster
4. Almost all are solids†	4. Solids, liquids, or gases
5. Malleable (can be hammered into sheets)	5. Brittle in solid state
6. Ductile (can be drawn into wires)	6. Nonductile

**Except copper and gold.*

†Except mercury; cesium and gallium melt in a protected hand.



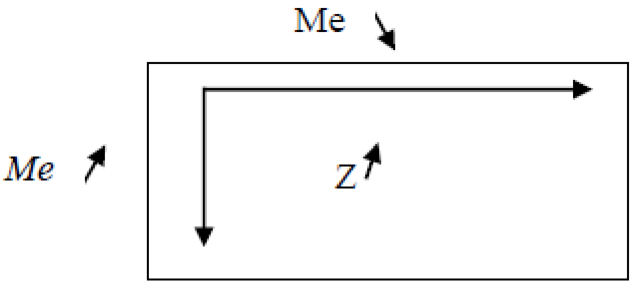
Some Chemical Properties of Metals and Nonmetals

Metals	Nonmetals
1. Outer shells contain few electrons—usually three or fewer	1. Outer shells contain four or more electrons*
2. Form cations (positive ions) by losing electrons	2. Form anions (negative ions) by gaining electrons†
3. Form ionic compounds with nonmetals	3. Form ionic compounds with metals† and molecular (covalent) compounds with other nonmetals
4. Solid state characterized by metallic bonding	4. Covalently bonded molecules; noble gases are monatomic

**Except hydrogen and helium.*

†Except the noble gases.

- χdecreases from left to right across a period due to increasing Z.
- χincreases down a column of the periodic table.



CHAPTER 6.

CHEMICAL BONDS

Chapter contents

- **The covalent bond in Lewis's theory,**
- **The polarized covalent bond, dipole moment and partial ionic character of the bond,**
- **Geometry of molecules: Gillespie theory or VSEPR,**
- **Chemical bonding in the quantum model**

I. Introduction

A chemical bond is the attractive force that binds atoms together in a molecule, or a crystal lattice. If a system has a lower energy when the atoms are close together than when apart, then bonds exist between those atoms. A bond is an electrostatic force that holds the atoms of elements together in a compound. There are three types of bonding:

- **Intramolecular bonds**: ionic, covalent, and metallic bonds
- **Intermolecular bonds**: hydrogen bonding, Van der Waal's forces

II. Ionic bonding

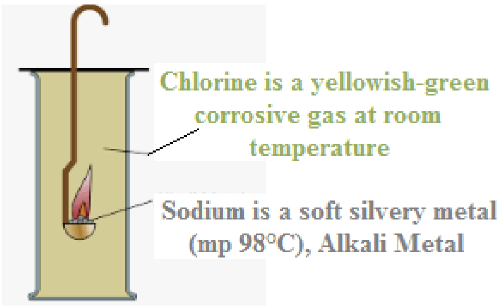
An ionic bonding, results from the transfer of electrons from a metal to a nonmetal

We recall that an ion in which the atom or group of atoms has fewer electrons than protons is **positively charged**, and is called a **cation;** one that has more electrons than protons is **negatively charged**, and is called an **anion.**

Note that hydrogen can form both a cation, **H^+ (hydrogen ion)** as in **HCl**, or **an anion H^- (hydride ion)** as in **NaH**.

An ion that consists of only one atom is described as a **monatomic ion.** Examples include the chloride ion, Cl^- , and the magnesium ion, Mg^{2+}. An ion that contains more than one atom is called a **polyatomic ion.** Examples include the ammonium ion, NH_4^+ ; the hydroxide ion, OH^- ; and the sulfate ion, SO_4^{2-}. The atoms of a polyatomic ion are held together by covalent bonds.

Consider the reaction of sodium Na (a Group I_A metal) with chlorine Cl (a Group V_{IIA} nonmetal). Both sodium and chlorine react with water, sodium vigorously. By contrast, sodium chloride is a white solid (mp 801°C) that dissolves in water with no reaction and with the absorption of just a little heat.

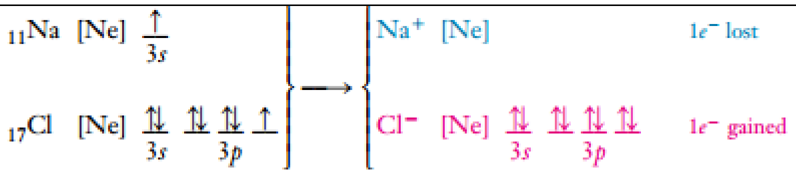


$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Sodium Chlorine Sodium Chloride

We can understand this reaction better by showing electron configurations for all species.

We represent chlorine as individual atoms rather than molecules, for simplicity.



In this reaction, Na atoms **lose one electron** each to form Na^+ ions, which contain only 10 electrons, the same number as the ***preceding*** noble gas, **neon**. **We say that sodium ions have the neon electronic structure**: Na is **isoelectronic** with Ne. In contrast, Cl atoms **gain one electron** each to form Cl^- ions, which contain 18 electrons. This is the same number as the ***following*** noble gas, **argon**; Cl is **isoelectronic** with Ar.

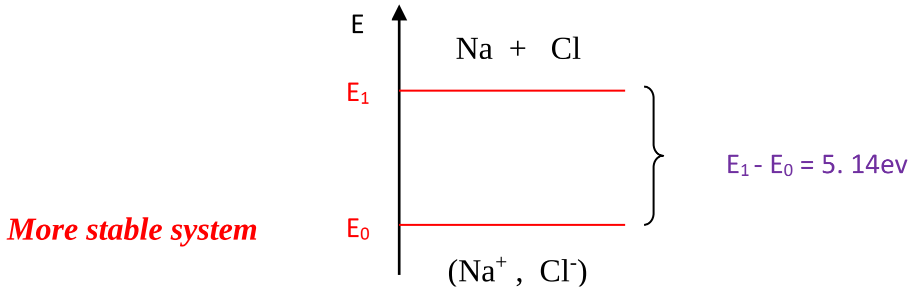
$$_{11}Na : 1s^22s^22p^63s^1 \;:\; {}_{10}[Ne]3s^1 \;\Rightarrow\; {}_{11}Na^+ : {}_{10}[Ne]3s^0 \equiv {}_{10}[Ne]$$

$$_{17}Cl : 1s^22s^22p^6\,3s^23p^5 : {}_{18}[Ne]\,3s^23p^5 \;\Rightarrow\; {}_{17}Cl^- : {}_{18}[Ne]\,3s^23p^6 \equiv {}_{18}[Ar]$$

These processes can be represented compactly as:

$$Na \rightarrow Na^+ + e^- \qquad \text{and} \qquad Cl + e^- \rightarrow Cl^-$$

The energy associated with the attraction of separated gaseous positive and negative ions to form an ionic solid is the ***crystal lattice energy*** of the solid. For NaCl, this energy is **-789 kJ/mol**; that is, one mole of NaCl solid is 789 kJ lower in energy (***more stable***) than one mole of isolated Na^+ ions and one mole of isolated Cl^- ions. We could also say that it would require 789 kJ of energy to separate one mole of NaCl solid into isolated gaseous ions.



1- Bond Length

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. You learned that the energy of the electrostatic attraction (***E_{att}***), a measure of the force’s strength, is inversely proportional to the internuclear distance between the charged particles (r):

$$\boxed{E_{att} = \frac{-e^2}{r}}$$

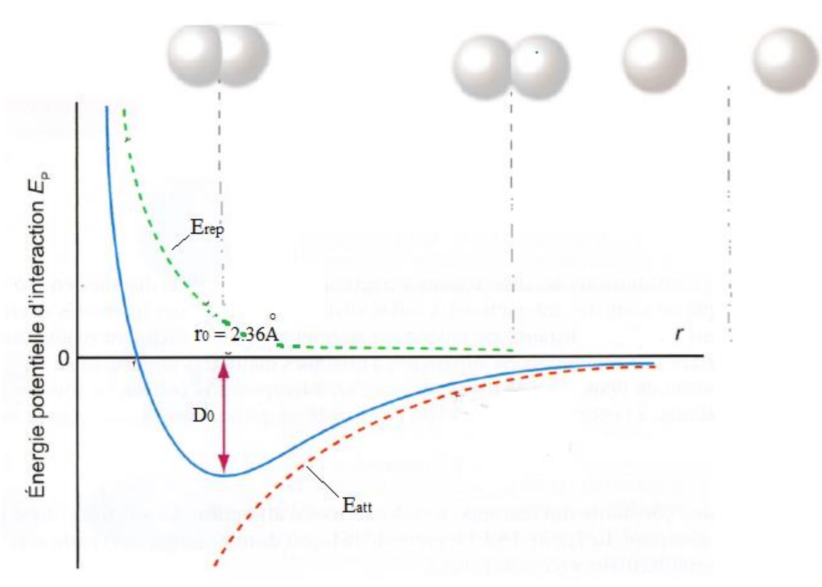
Where each ion's charge is represented by the symbol ***e***. The proportionality constant ***k*** is :

$$k = 2.31 \times 10^{-28}\ \mathrm{J{\cdot}m}$$

If the ions have opposite signs (as in NaCl, for example, where the charge is +1 for Na^+ and −1 for Cl^-), then **E_{att} is negative**, which means that :

Energy is released when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

As shown by the red curve in the lower half of the Figure below.



A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na", predicts that the maximum energy is released when the ions are infinitely close to each other, at *r* = 0. Because ions occupy space, however, they cannot be infinitely close together.

At very short distances, repulsive electron–electron interactions between electrons E_{rep} on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the green curve in the upper half of the Figure.

$$\boxed{E_{rep} = be^{-ar}}$$

The total energy of the system is a balance between the attractive and repulsive interactions.

$$\boxed{E = E_{att} + E_{rep} = \frac{-e^2}{r} + be^{-ar}}$$

The purple curve in the figure shows that the total energy of the system reaches a minimum at r_0.

r_0 is the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured **bond Length**.

Energy is released when a bond is formed.

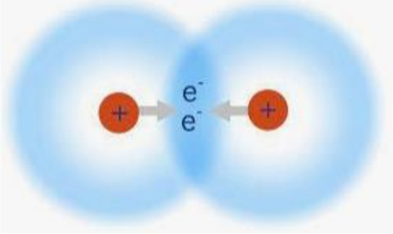
And r_0 is given by the following equation:

$$\boxed{r_0 = r_{Na^+} + r_{Cl^-}}$$

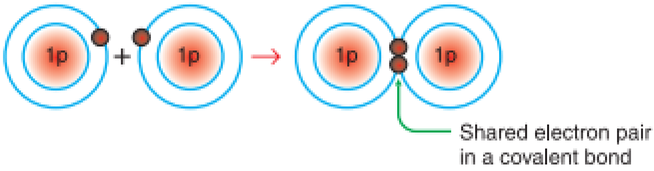
III. The covalent bonding in Lewis's theory

A covalent bond, the most common kind of chemical bond, results when two atoms *share* some (usually two) electrons. Many molecules are formed when outermost shell or valence electrons are shared between two atoms. This sharing of electrons creates a covalent bond.

Covalent bond formation can be illustrated by the sharing of electrons between two hydrogen atoms with the electronic configuration H: $1S^1$ to form a molecule of hydrogen.



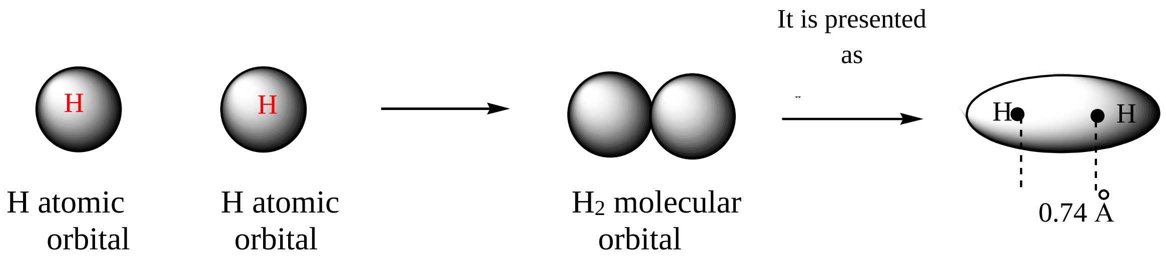
In the hydrogen molecule, each hydrogen atom attains the stable electron configuration of helium $1S^2$.



$H\bullet\!\!-\!\!\bullet H \quad \rightarrow \quad 1S^2 \equiv He$ **Stable electron configuration**

Unlike an ionic bond, the electron clouds of the two ions that make up the molecule do not interfere with each other, but in the case of a covalent bond, they overlap, the length of the bond in the H_2 molecule is equal to 0.74 Å and it is smaller than the sum of the radii of the two hydrogen atom ($r_H = 0.53$ Å) which is $2r_H = 1.06$ Å.

The representation of the covalent bond is as follows:



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➢ Lewis Formulas

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol.

You can represent the formation of the covalent bond in H_2 from atoms as follows:

$$H\cdot + \cdot H \rightarrow H:H$$

This uses the Lewis electron-dot symbol for the hydrogen atoms and represents the covalent bond by a pair of dots.

The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

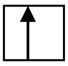
Lewis Symbols

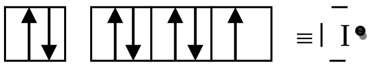
1. Electrons are represented as DOTS.
2. Only VALENCE electrons are used.
3. Draw a first tentative structure: Frequently the central element is the one with least atoms in the molecule. In your first draft, attach the atoms with single bonds.
4. Add electrons as dots to get octets around atoms: Each atom must have its valence shell completely filled. Remember to count bonds and lone electrons.

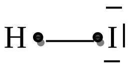
5. Count the total number of electrons: Ensure the number of electrons displayed in the symbol agree with the calculation from step 1.

Exemple

molecule of HI

H : $1s^1$  ≡ H •

$_{53}$I : $_{36}$[Kr]$4d^{10}5s^25p^5$ 



I. The polarized covalent bond

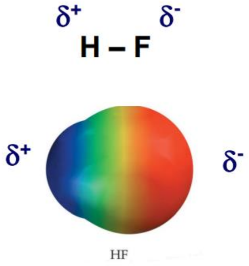
Covalent bonds can have ionic character, these are polar covalent bonds. A chemical bond in which the electrons are not shared equally due to differences in the electronegativity of the atoms.

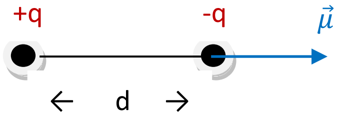
1- Dipole moment

Two separated charges of opposite sign, $q_1 = -q$ and $q_2 = +q$ form an electric dipole. The dipole moment $\vec{\mu}$ is defined by:

$$\|\vec{\mu}\| = |q|d$$

where q is the charge and d define the position of the two charges in space.





In the SI system, the unit of the electric dipole moment is **Coulomb·meter**. Since these units result in very small numbers, however, the unit **Debye** (**$1D = 3.33564 \cdot 10^{-30}$ C.m**) is often used.

2- partial ionic character of the bond

As long as atom A differs from atom B in electronegativity, two poles appear resulting from two partial charges, which we symbolize $+\delta$ and $-\delta$ and :

$$|\delta| < |e|$$

So, an electric dipole is produced by the two charges $+\delta$ and $-\delta$ on the molecule AB which has a dipole moment μ, where:

$$\boxed{\mu = |\delta| \cdot r}$$

Where **r** is the distance between the atoms A and B.

In the case of an ionic bond, the electric dipole consists of two elemental charges +e and –e, and the dipole moment in this case is given by:

$$\boxed{\mu_i = |e| \,.\, r}$$

According to general convention, the dipole moment points from the center of the negative charge distribution to the center of the positive one. If the two centers do not coincide the molecule has a permanent dipole moment.

The ionic character **P** describes partially ionic chemical bonds:

$$\boxed{P = \frac{\mu}{\mu_i} \,.\, 100}$$

Where μ is the experimentally measured dipole moment and μ_i is the dipole moment of an ionic bond.

$$P = \frac{\mu}{\mu_i} \,.\, 100 \quad = \frac{|\delta|\,.r}{|e|\,.r} \,.\, 100 \quad \Rightarrow \quad \boxed{P = \frac{|\delta|}{|e|} \,.\, 100}$$

II.Geometry of molecules: Gillespie theory or VSEPR

The premise of VSEPR is that the valence electron pairs surrounding an atom tend to repel each other. The greater the repulsion, the higher in energy (less stable) the molecule is. Therefore, the VSEPR-predicted molecular geometry of a molecule is the one that has as little of this repulsion as possible. Gillespie has emphasized that the electron-electron repulsion due to the Pauli Exclusion Principle is more important in determining molecular geometry than the electrostatic repulsion.

The "AXE method" of electron counting is commonly used when applying the VSEPR theory. The electron pairs around a central atom are represented by a formula **AX_nE_m**.

where *A* represents the central atom and always has an implied subscript one. Each *X* represents a ligand (an atom bonded to A). Each *E* represents **a *lone pair*** of electrons on the central atom. The total number of *X* and *E* is known as the steric number. For example in a molecule AX_3E_2, the atom A has a steric number of 5.

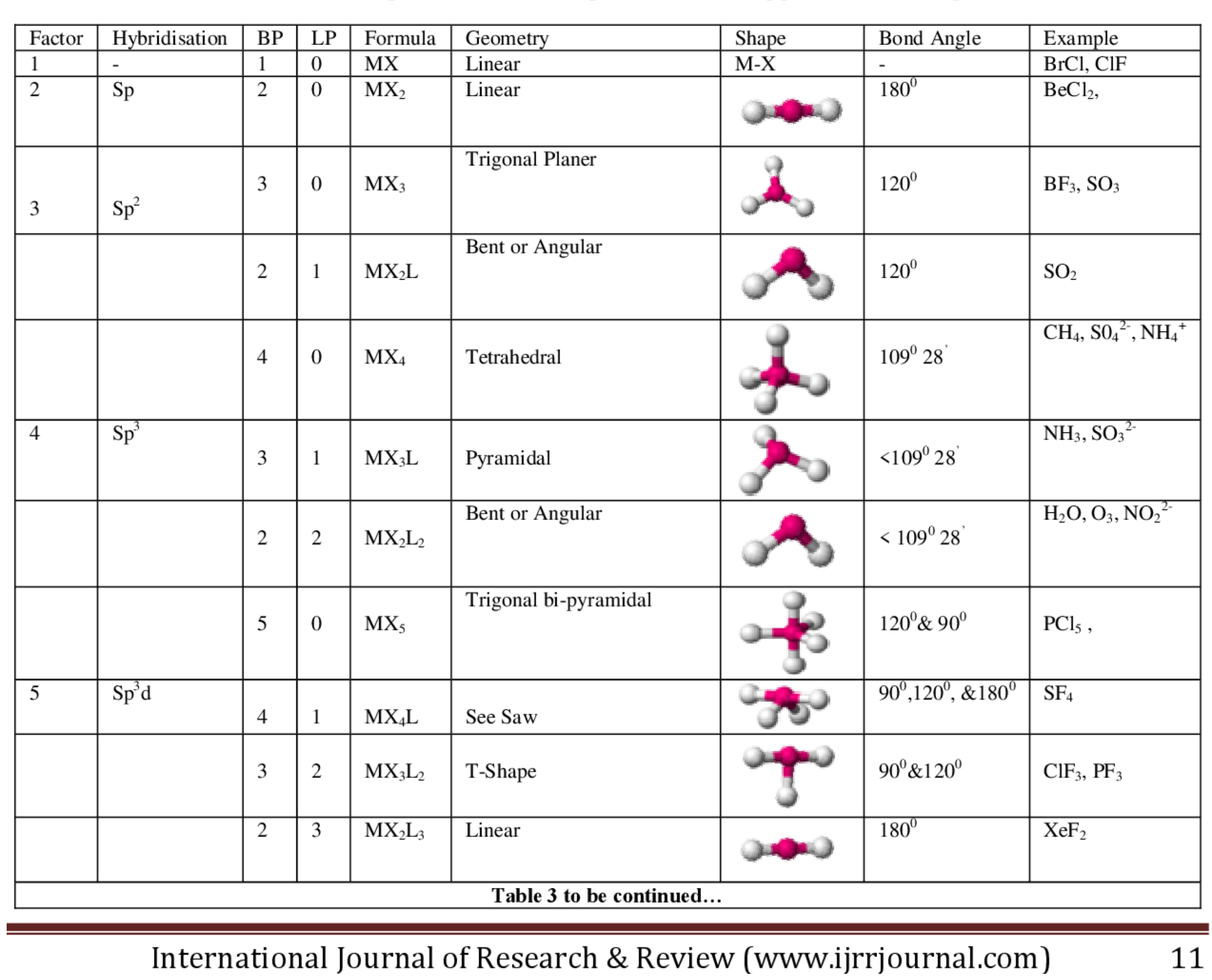


Table 3: The description of molecular shape: (BP - Bonding pair and LP - Lone pair)

Factor	Hybridisation	BP	LP	Formula	Geometry	Shape	Bond Angle	Example
1	-	1	0	MX	Linear	M-X	-	BrCl, ClF
2	Sp	2	0	MX_2	Linear		180^0	$BeCl_2$,
3	Sp^2	3	0	MX_3	Trigonal Planer		120^0	BF_3, SO_3
		2	1	MX_2L	Bent or Angular		120^0	SO_2
4	Sp^3	4	0	MX_4	Tetrahedral		$109^0\ 28^{'}$	CH_4, $S0_4^{2-}$, NH_4^+
		3	1	MX_3L	Pyramidal		$<109^0\ 28^{'}$	NH_3, SO_3^{2-}
		2	2	MX_2L_2	Bent or Angular		$< 109^0\ 28^{'}$	H_2O, O_3, NO_2^{2-}
5	Sp^3d	5	0	MX_5	Trigonal bi-pyramidal		120^0& 90^0	PCl_5 ,
		4	1	MX_4L	See Saw		90^0,120^0, &180^0	SF_4
		3	2	MX_3L_2	T-Shape		90^0&120^0	ClF_3, PF_3
		2	3	MX_2L_3	Linear		180^0	XeF_2

Table 3 to be continued…

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III. Chemical bonding in the quantum model

1- Molecular orbitals

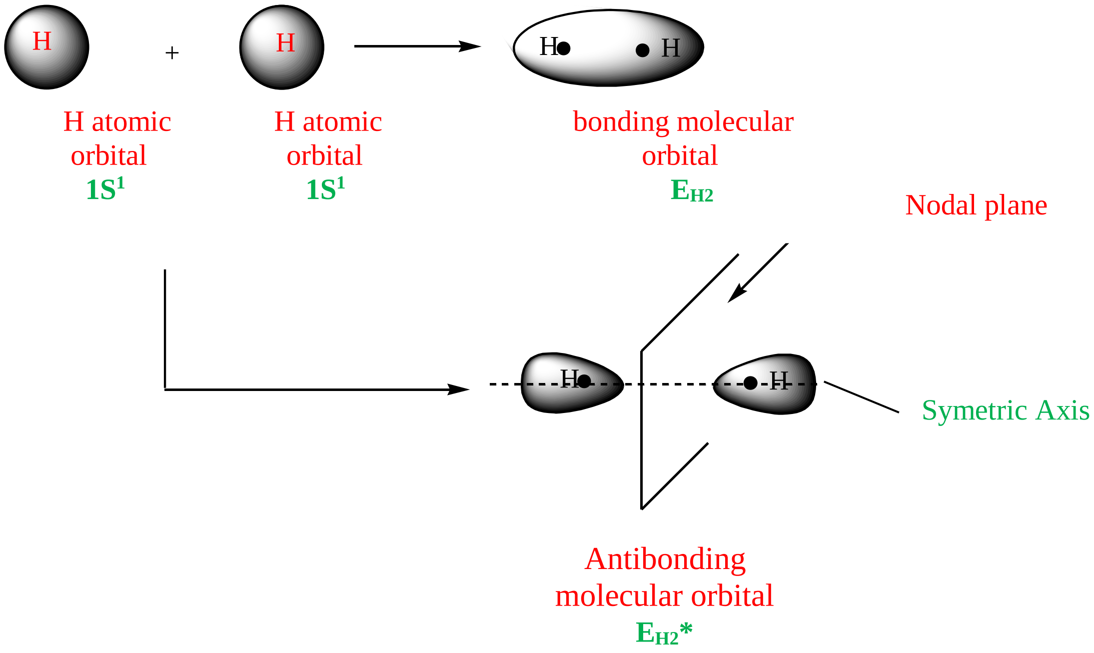
In wave mechanics a H_2 molecule is a $1S^2$ molecular station formed when two $1S^1$ atomic stations of two hydrogen atoms H combine.

H• + •H → H•—•H

atomic orbital $1S^1$ atomic orbital $1S^1$ molecular orbital $1S^2$

Two special energy values:

- The energy of the molecular bonding level E_{H2} : $E_{H2} < 2E_H = 2 . 13.6$ ev, and its corresponding molecular bonding orbital.
- The energy of the molecular antibonding level of te E^*_{H2} : $E^*_{H2}{}^* > 2E_H = -2 . 13.6$ ev And its corresponding molecular antibonding orbital.



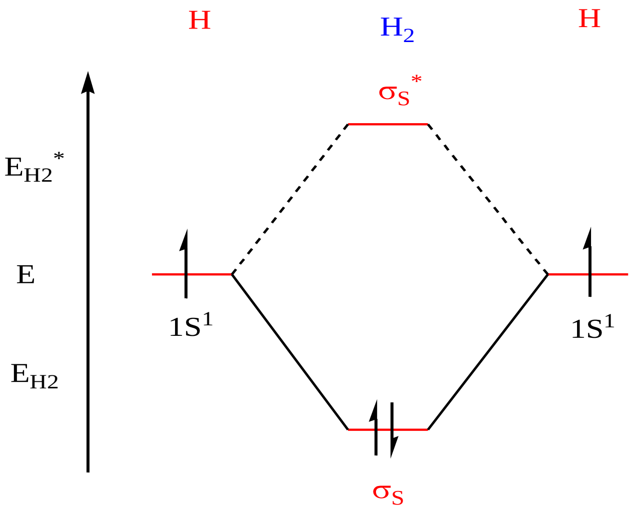
- **Bond order**

Bond order determines the number of bonds shared in a molecule and it is giving by the following equation :

$$\text{bond order} = \frac{1}{2}\left(\begin{array}{c}\text{number of electrons}\\ \text{in bonding MOs}\end{array} - \begin{array}{c}\text{number of electrons}\\ \text{in antibonding MOs}\end{array}\right)$$

- The higher the order of the bond, the stronger the bonding.
- The number of bonding and antibonding electrons is calculated based on the energy diagram of the molecule.

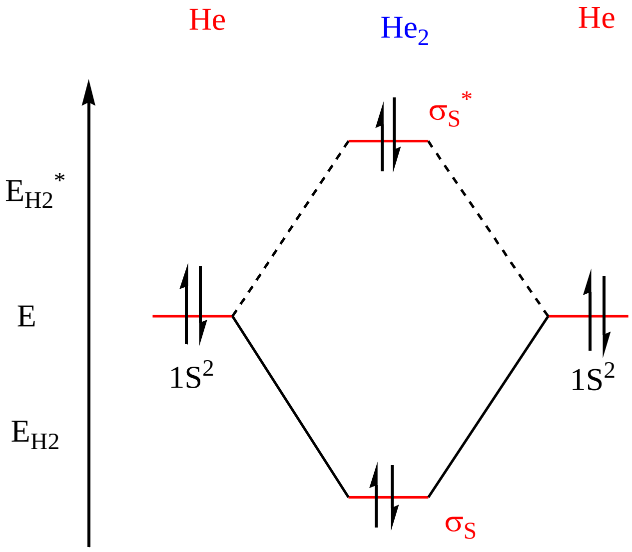
The H_2 molecule is represented on an energy diagram as follows:



From the diagram, we conclude that the number of bonding electrons = 2, the number of anti-bonding electrons = 0, and hence the bond order = 1. This means that in the H_2 molecule there is one covalent bond.

Exemple

Let the helium molecule be He_2. The energy diagram for this molecule is represented as follows:

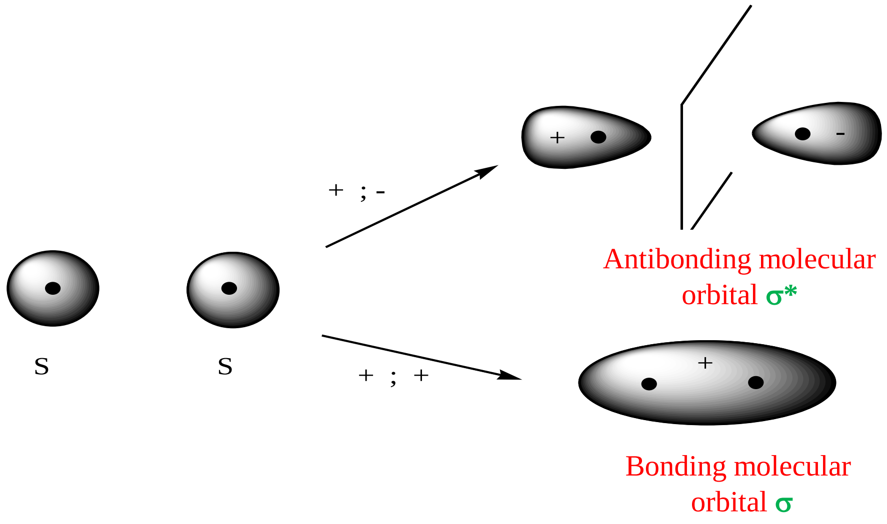


The number of bonding electrons is 2 and the antibonding number is 2, so the bond order in this case is 0. This means there is no He-He bond, meaning there is no He_2 molecule.

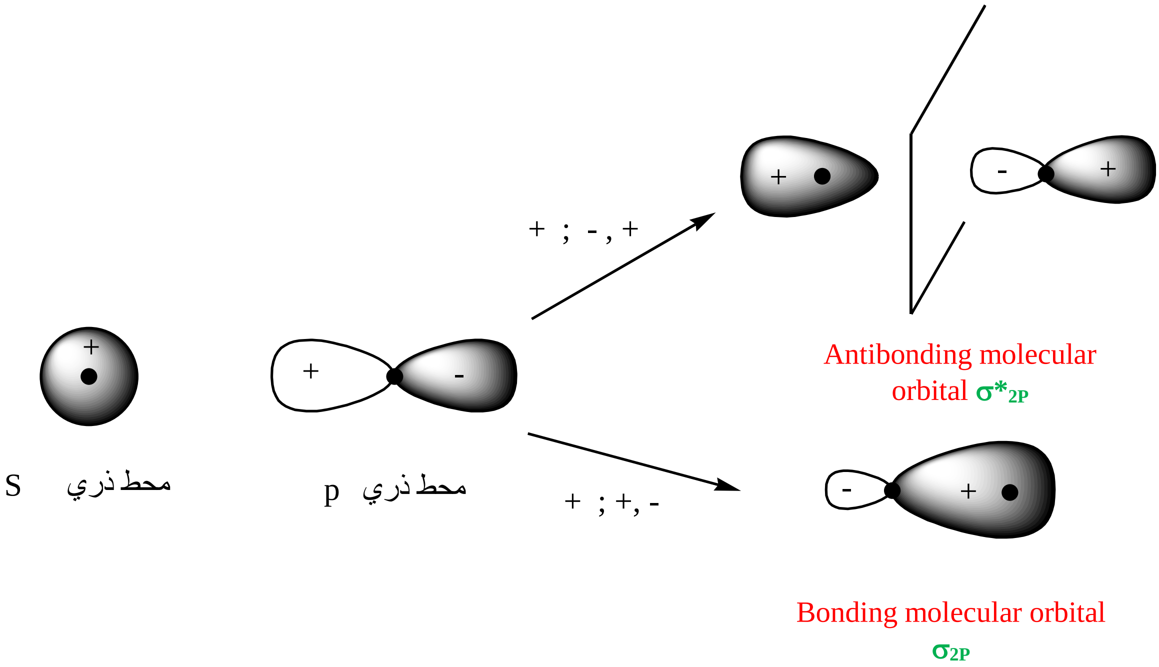
➢ Molecular orbitals σ and π

- ✓ We obtain molecular orbitals of type σ when the coverage of the atomic orbital is according to an axis (axial coverage).

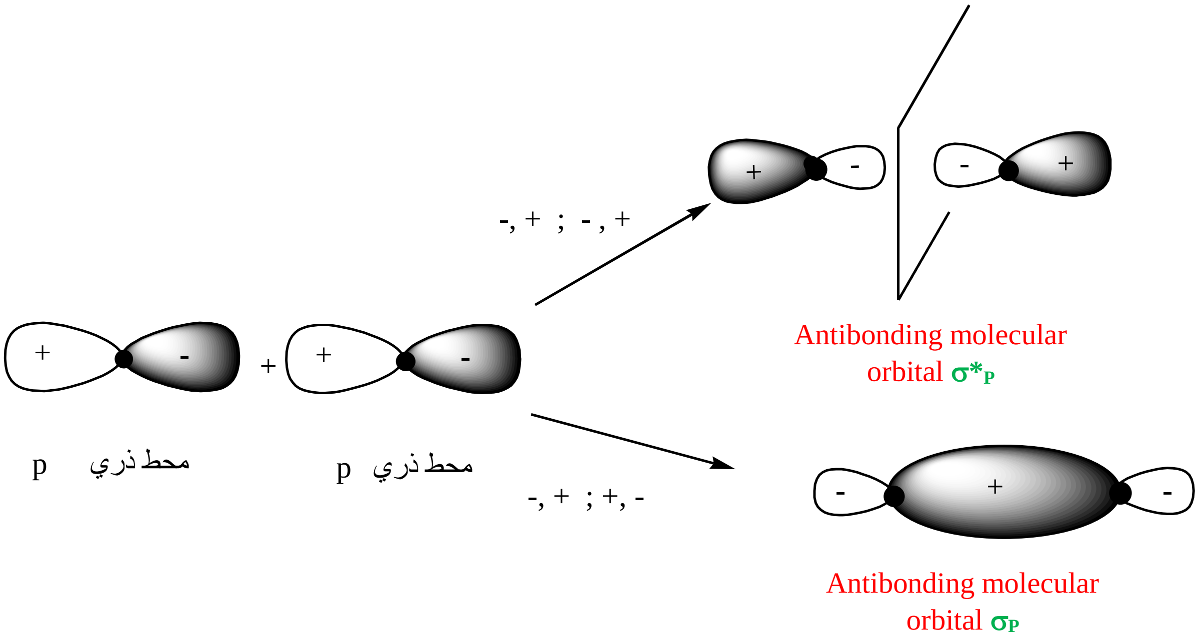
In simple molecules, we obtain an axial coverage between two atomic centers S of two different atoms as follows:



Or an axial coverage between an atomic orbital S and an atomic orbital P for two different atoms as follows:



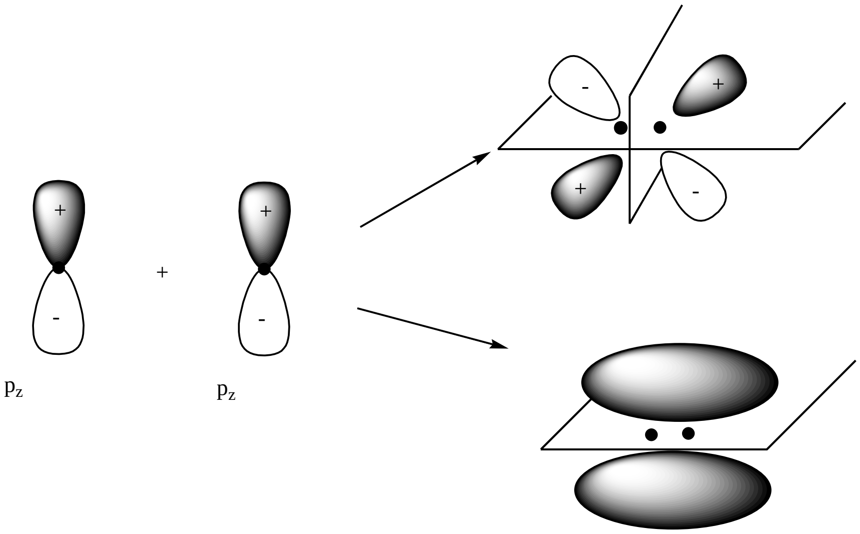
Or an axial coverage between two atomic orbital P for two different atoms as follows:



- ✓ We obtain molecular orbital of type π when the coverage of the atomic orbitals is according to the level (lateral coverage). We obtain it only in the case of p-type atomic stations.

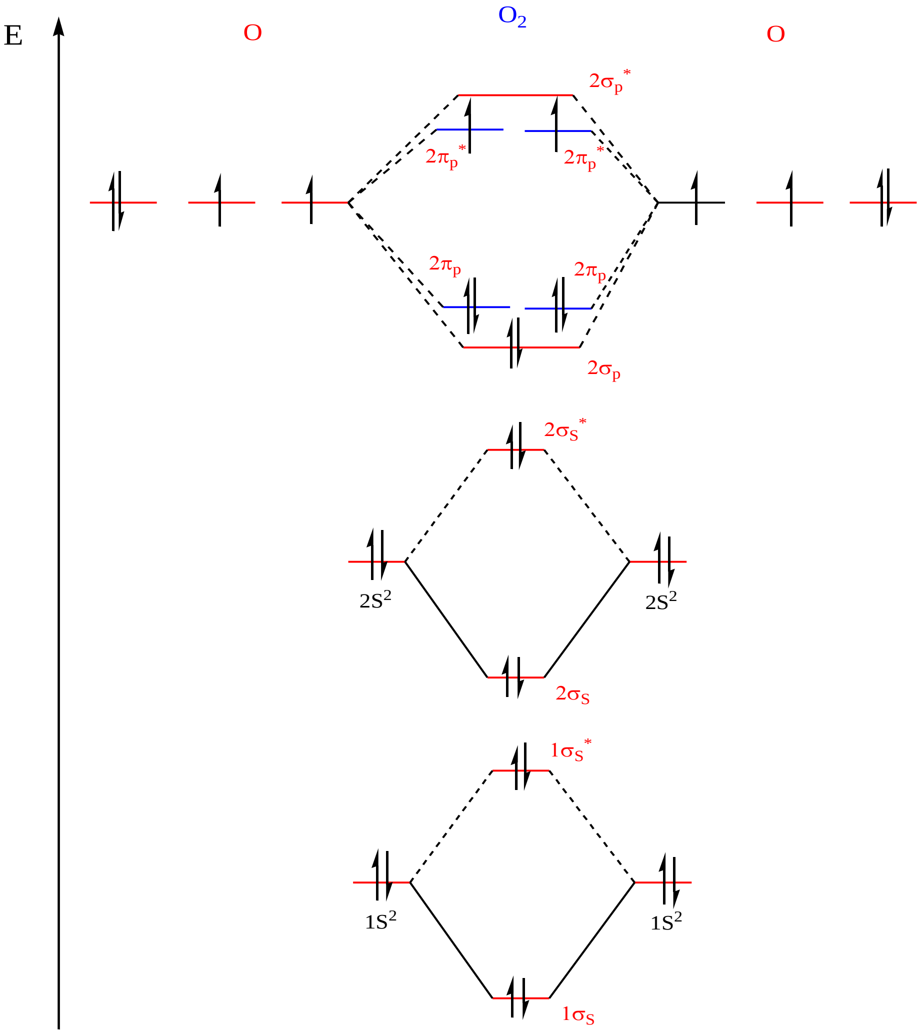
When two atoms combine, the atomic station p_y of the two atoms gives:

- Axial coverage, we get two molecular orbitals σ_p and σ_p*. As for the atomic orbital p_x and p_z, they give lateral coverage, so we get two molecular orbitals π.



Representation of the energy diagram for molecules with similar nuclei A2

Let see the exemple of O_2 . $_8O : 1s^2 2s^2 2p^4$



- Electrons are distributed according to the Hund and Bole rule.
- The bond order of the O_2 molecule is 4/2 = 2.

- The electronic configuration of the oxygen molecule is written in the form:

$$O_2 : (1\sigma_s)^2(1\sigma_s^*)^2(2\sigma_s)^2(2\sigma_s^*)^2(2\sigma_p)^2(2\pi_p)^4(2\pi_p^*)^2$$

Note that : In some A_2 molecules, the energy of the molecular orbital $2\sigma_p$ is greater than the energy of the molecular orbital $2\pi_p$, and this is due to the closeness of the energy levels in the element.

Example of the nitrogen molecule N_2.

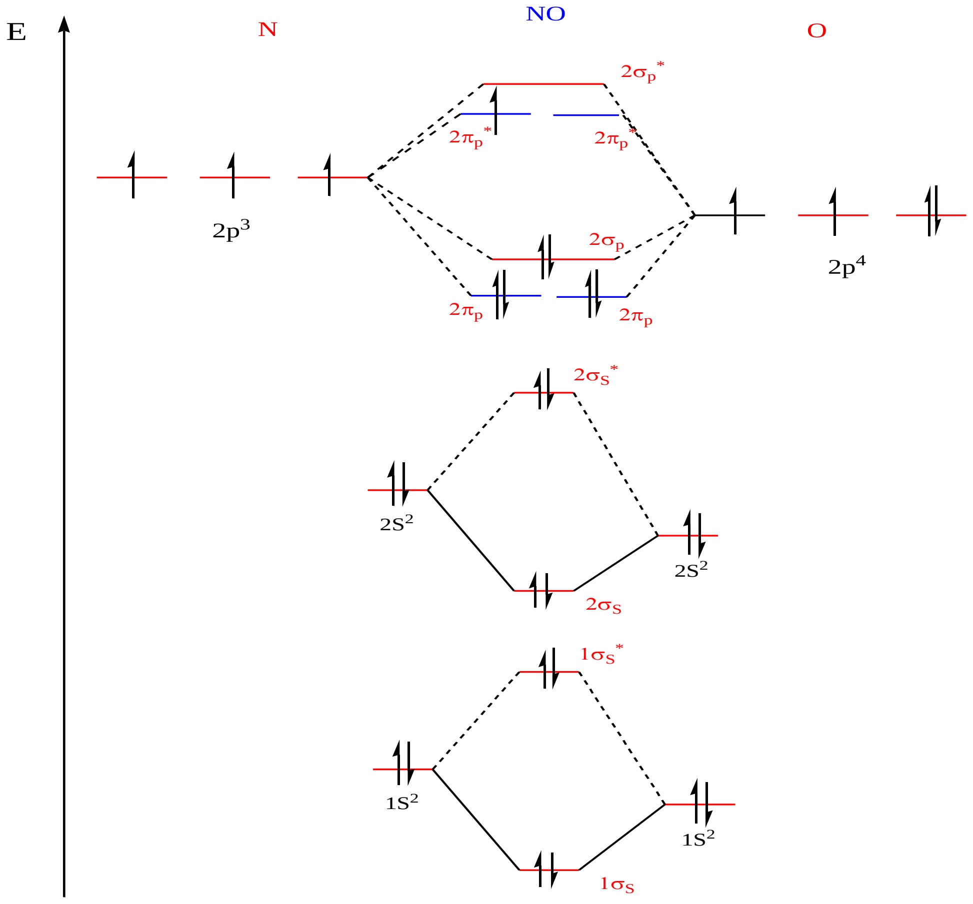
$$N_2 : (1\sigma_s)^2(1\sigma_s^*)^2(2\sigma_s)^2(2\sigma_s^*)^2(2\pi_p)^4(2\sigma_p)^2$$

- **The electronic structure of molecules with dissimilar nuclei AB**

Let's take the example of the NO molecule

The electronegativity of oxygen is greater than that of nitrogen, and therefore the energy under the atomic layers of element O is less than that of element N.

$_7N : 1s^2 2s^2 2p^3$ ↑↓ ↑ ↑ ↑ $_8O : 1s^2 2s^2 2p^4$ ↑↓ ↑↓ ↑ ↑



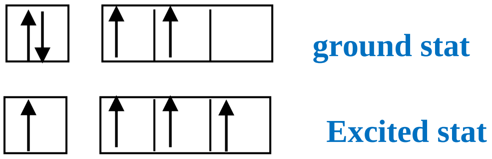
$NO : (1\sigma_s)^2(1\sigma_s^*)^2(2\sigma_s)^2(2\sigma_s^*)^2(2\sigma_p)^2(2\pi_p)^4(2\pi_p^*)^1$

Bond order of NO = 2.5

2- Hybridization of atomic orbitals - molecular geometry -

Carbon in its basic state has a valence of 2, but when it binds to other elements, its valence becomes 4, which results from the hybridization of atomic orbitals. There are different hybridization states, each of which gives the geometric structure of orbitals in space.

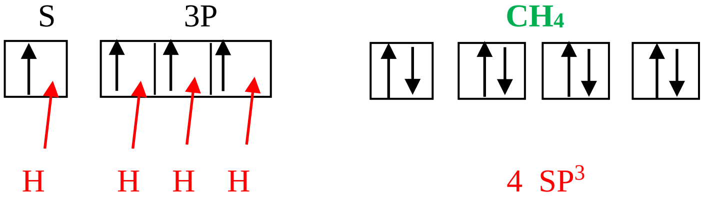
$^{12}_{6}C : 1S^22S^22P^2 \equiv [He]\ 2S^22P^2 \equiv$



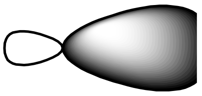
a) Hybridization sp³

Experimental results showed that the methane molecule has four equal bonds, the angles $(\widehat{HCH})$ is all equal to **109.28°**, and the C–H bonds have the same length of **1.093 Å**.

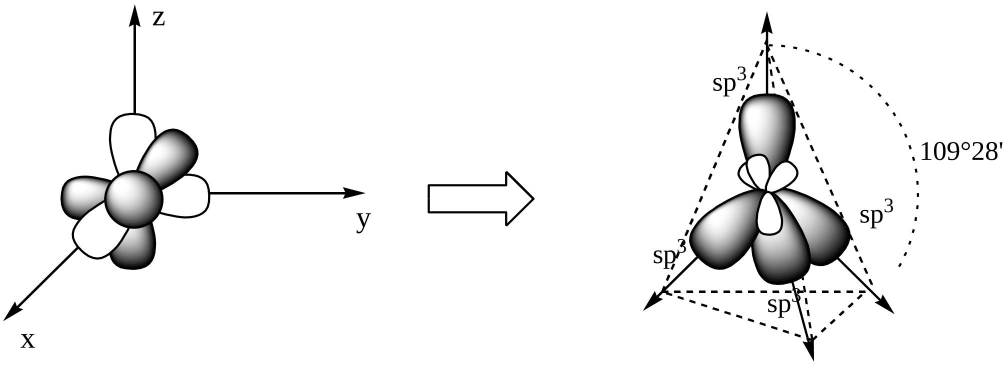
Methane is produced by combining an S atomic orbital with **three** P atomic orbitals, giving four SP^3 hybrid molecular orbitals.



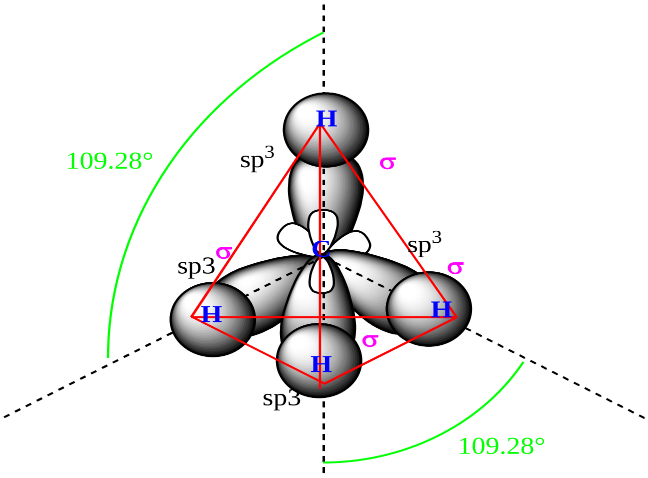
Take the shape as follow



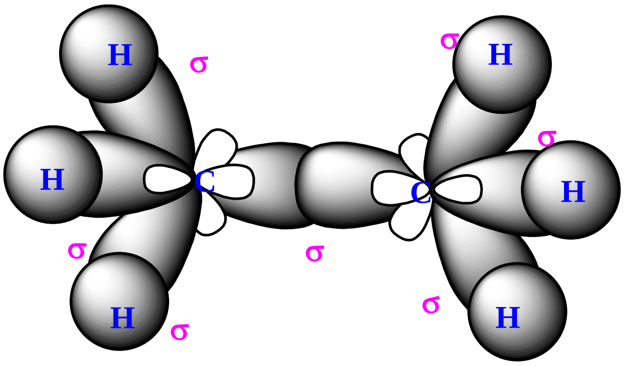
These orbitals are oriented according to a **tetrahedron** (a pyramid with a triangular base). The angle between the axes of this quadrilateral is **109.28°.**



result orbitals **SP^3** from an axial covering between an S atomic orbital and three P atomic orbitals, which leads to the formation of σ type bonds.

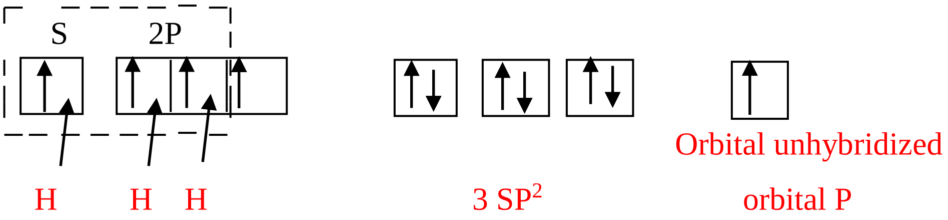


Exemple : $CH_3—CH_3$

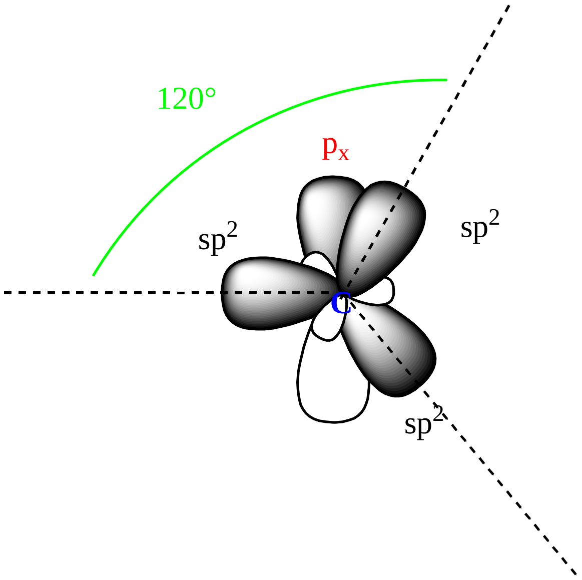


b) Hybridization sp^2

Results by combining of an S atomic orbital with two atomic orbitals P, giving three SP^3 hybrid molecular orbitals.

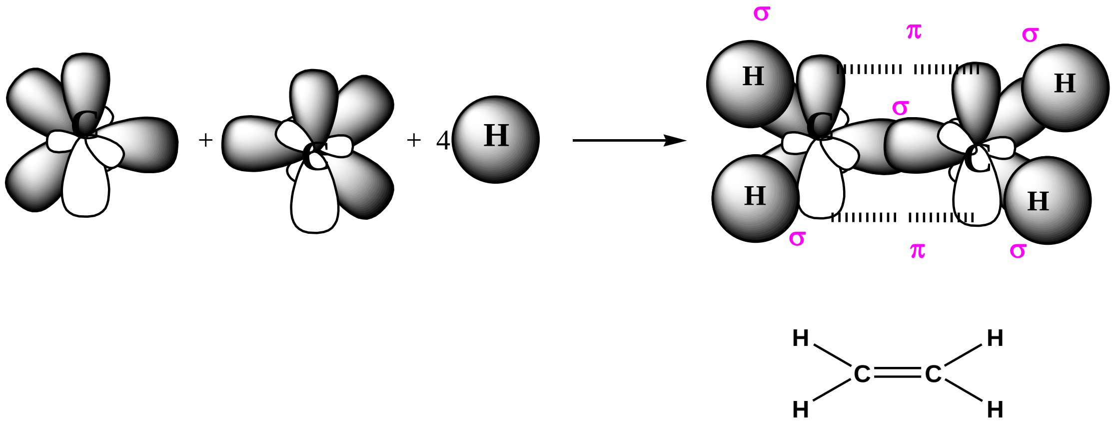


These orbitals are oriented in the plane. The angle between these axes is **120°**. The lateral coverage between the unhybridized P-atomic arbitrates of the two carbons produces a π bond .



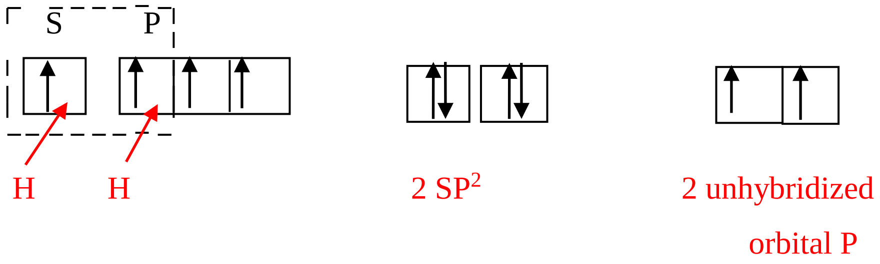
Exemple

$CH_2 = CH_2$

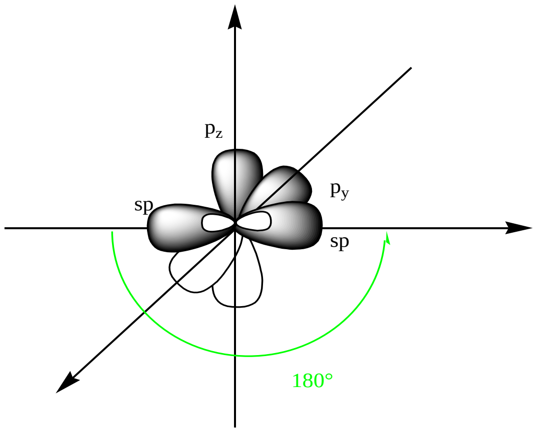


c) Hybridization sp^2

Results by combining of an S atomic orbital with one atomic orbitals P, giving **two** SP^3 hybrid molecular orbitals.

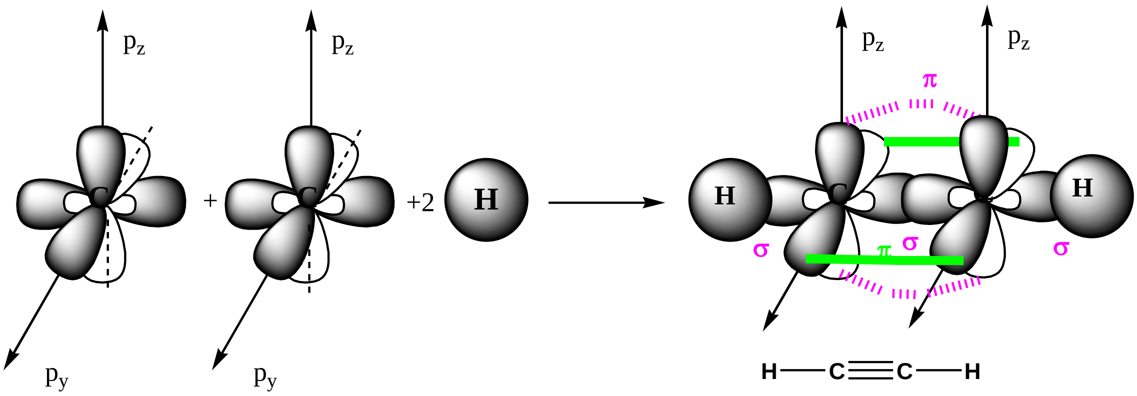


The orientation of the two hybrid orbitals is linear, and the angle between the axes is **180°**. The lateral coverage between the two unhybridized P atomic arbitrates of the two carbons produces **two π** bonds.



Exemple

CH ≡ CH



in general

- ✓ If an atom inside a molecule has **four σ** bonds, then this atom is **sp^3 hybridized**.
- ✓ If an atom inside a molecule has **three σ** bonds and **one π** bond, then this atom is **sp^2 hybridized**.
- ✓ If an atom inside a molecule has **two σ** bonds and **two π** bonds, then the this atom is **sp hybridized**.
- ✓ The free electron pair of an atom is considered as a σ bond

1. بروفيسور ف.جازي; دروس SEC100 سنة اولى جذع مشترك DES جامعة بسكرة; 1996
2. R. Ouahes, B. Devallez, chimie génerale, SNED, Alger, 1974 .
3. McMurry Fay ; Chemistry_Fourth Edition.
4. The Foundations of Chemist ; General_Chemistry_whitten full.pdf.
5. General Chemistry Principles, Patterns, and Applications. http://www.saylor.org/books.
6. Darrell D. Ebbing; Steven D. Gammon., General Chemistry. 9th Edition. 2009 by Houghton Mifflin Company.
7. Raymond Chang ; General Chemistry *The Essential Concepts;* Fifth Edition. McGraw-Hill Companies. 2008.
8. R. Nelson Smith ; Conway Pierce., Solving General Chemistry Problems, FIFTH EDITION . W. H. FREEMAN AND COMPANY San Francisco. 1980.