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شهادة ادارية

المصادقة على تقرير خبير للموافقة على مطبوعة جامعية

بعد الإطلاع على تقارير لجنة الخبراء للموافقة على المطبوعة البيداغوجية للأستاذ : : **جحيش المختار– أستاذ محاضر أ**، بالقاعدة المشتركة بكلية التكنولوجيا بجامعة محمد بوضياف بالمسيلة والتي كانت كلها ايجابية ، تمّ تقرير التّالي:

1– المصادقة على تقارير لجنة الخبراء للموافقة المطبوعة البيداغوجية والمعنونة بــ:

Structure of Matter
First year ST and Renewable Energy students

2– حيث تمّ تشكيل هذه اللجنة بناء على اجتماع المجلس العلمي للكلية المنعقد بتاريخ 2024/06/25 المكونة من السّادة الآتية أسماؤهم:

- **لفحل مصطفى**، أستاذ محاضر قسم أ، جامعة قسنطينة 3
- **لكحل هشام**، أستاذ محاضر "أ"، جامعة محمد بوضياف– المسيلة
- **مخلوفي الهاني**، أستاذ محاضر "أ"، جامعة محمد بوضياف– المسيلة

وتمت الموافقة بالاجماع على هذه المطبوعة.

رئيس المجلس العلمي للكلية

المجلس العلمي

د. علي جريوي

People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

University of Mohamed Boudiaf-M'sila

Faculty of Technology

Department of base common

Structure of Matter

Program for first-year ST and Renewable Energy students

Course handout by: Dr. Mokhtar DJEHICHE

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Foreword

This manuscript represents the culmination of five years of teaching experience in the Technical Science Department at the University of Mohamed Boudiaf in M'sila. This document is primarily composed of course and application exercises, has been designed for first-year students enrolled in the renewable energies programs. This manuscript is in accordance with the recently revised curriculum for the course entitled "Elements of Chemistry," as established by the Pedagogical Committee of the Science and Technology Domain (CPND-ST). It is presented in the form of six chapters, which are respectively named as follows:

1. Fundamental concepts
2. Main Constituents of Matter
3. Radioactivity
4. Electronic Structure of the Atom
5. Periodic Classification of Chemical Elements
6. Chemical Bonds.

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I. Fundamental concepts

I.1. The matter

Everything occupies space and has mass (oceans, air and rocks), we are made of matter.

I.2. State of matter: Matter occurs, mainly, in three physical states: **the solid state, the liquid state and the gaseous state** , however, there are other unstable states such as the plasma state and the supercritical state (Figure I.1).

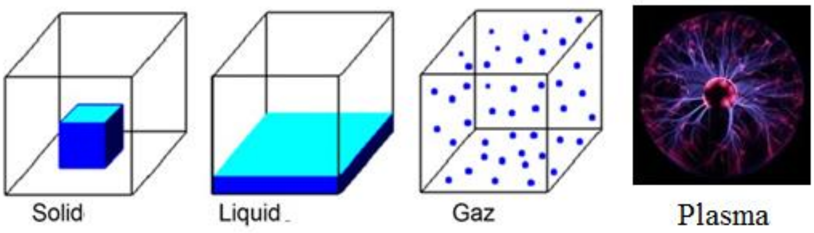


Figure I.1: States of matter

I.2.1. Solid state

In a solid, atoms are very close together, held in position by strong interatomic electrostatic forces (a high cohesion). They have some kinetic energy, which makes them vibrate around an equilibrium position, but they cannot change place (Figure I.2) . This means that solids have a fixed shape and a fixed volume, so they are rigid .

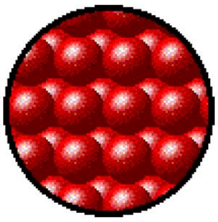


Figure I.2: Solid state form

I.2 .2. Liquid state

In a liquid, the atoms are not much further apart than in a solid. There are still quite strong interatomic bonds. The atoms have more kinetic energy and they are able to move randomly

(Figure I.3). There is less order than in a solid. Thus a liquid does not have a fixed shape, so it does not occupy a fixed volume.

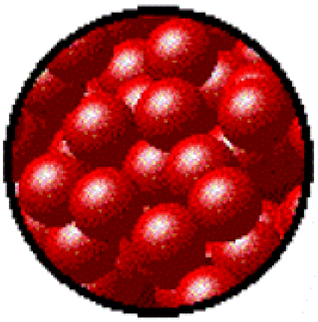


Figure I.3: Liquid state form

I. 2.3. Gaseous state

In a gas, atoms move randomly at high speeds. They are much more spaced apart than in a solid or liquid. There are no interatomic forces between the atoms. Interaction occurs only when atoms (or molecules) collide (Figure I.4). The internal energy of a gas is entirely kinetic.

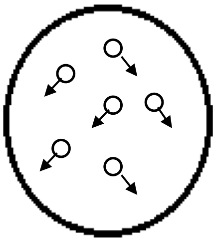


Figure I.4: Gas state form

I. 2.4. Supercritical state

A supercritical fluid is a unique state of matter that exists beyond a substance's critical point. This critical point marks the temperature and pressure at which the distinctions between liquid and gas phases disappear (Figure I.5).

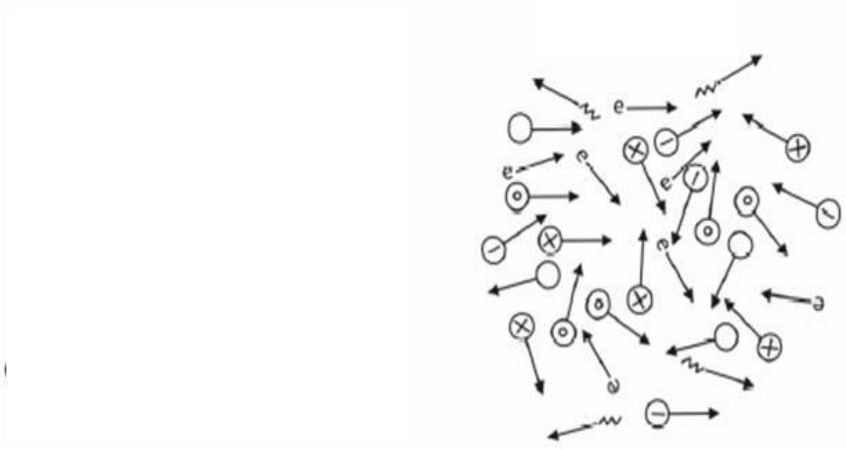


Figure I.5: plasma state form

1. 3. Change of state of matter

Changes of state are transitions between two physical states of matter. When a substance changes state, it does not transform into a new substance, for example: Ice water is still water; it is just water in a solid state.

Any substance can exist in any state, if it is cooled or heated sufficiently (Figure I.6). For example, if nitrogen gas is cooled to -195.79 °C, it turns into a liquid. If it is cooled further to -210 °C, it turns into a solid .

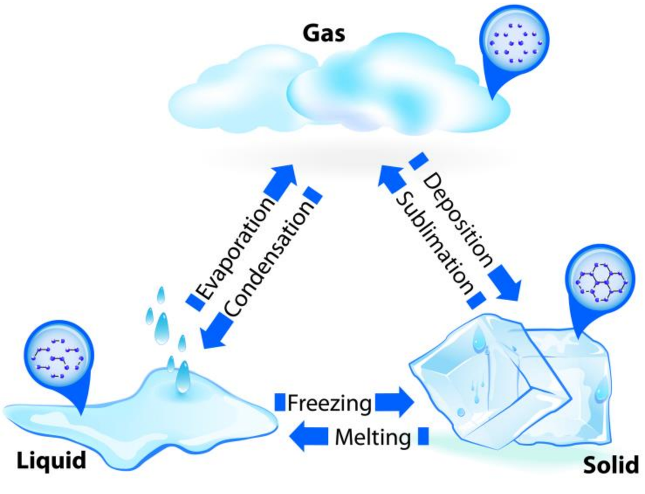


Figure I.6: Different states of matter and their transitions with plasma

I.4. Composition of matter

The state of matter can be an element, a compound or a mixture.

I.4.1. Elements

An element is a pure substance, It contains only one type of atom. Elements can be classified as metals, non-metals.

I.4.2. Compounds

A compound is a pure substance consisting of two or more elements combined in fixed proportions that contain more than one type of atom. A compound may contain charged particles (ions) or groups of atoms (molecules).

I.4.3. Mixtures

A mixture contains two or more substances; which may be elements or compounds of varying composition.

I.5. Concepts of atom and molecule

I.5.1. Atom

An atom (Ancient Greek [atomos], "unbreakable") is the smallest part of a simple body that can chemically combine with another. Atoms are infinitely small; if 35,000,000 copper atoms were placed end to end in a line, they would cover a distance of about 1 cm. By losing one or more electrons, an atom will become a positive ion or cation, and by gaining one or more electrons, it will become a negative ion or anion.

The atom is made up of a **nucleus** formed of nucleons (**protons and neutrons**), and an electronic procession formed of **electrons** (Figure I.7) .

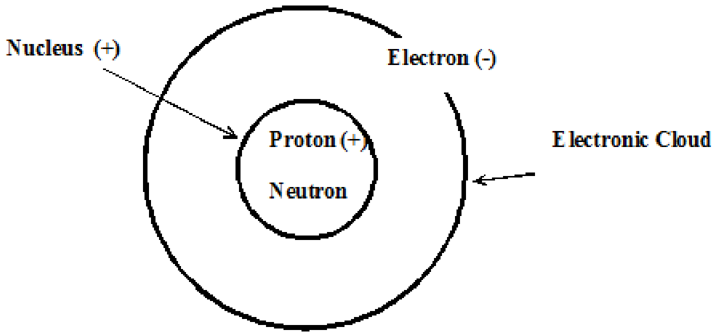


Figure I.7: A representative diagram of the atom

- *The nucleus:* constitutes the central part of the atom. The nucleus, very dense, is formed of a compact set of protons, positively charged particles and neutrons, neutral particles. The proton + neutron set called **nucleons**

- *The electron cloud:* it is made up of electrons which carry a negative electric charge exactly equal, in absolute value, to that of the proton.

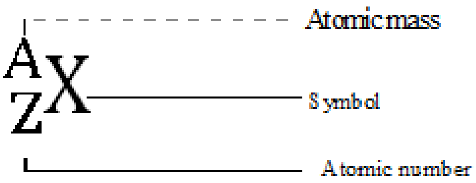
- *Atomic number Z*

The atom is electrically neutral. This means that it has as many positive charges (p+) as negative charges (e–). It therefore contains as many protons as electrons.

- *The mass number (A):*

Represents the number of nucleons, that is, the sum of the number of proton(s) and the number of neutron(s) constituting the nucleus of an atom.

The atom is symbolized by :



I.5.2. Isotope

Isotopes are atoms belonging to the same element, whose nuclei differ in the number of neutrons N. Isotopes therefore have the same Z, but a different mass number A.

Example

The simplest atom is the hydrogen atom whose nucleus contains a single proton and the electronic cloud a single electron: $_1^1H$

Three types of atoms have been identified whose nucleus contains only one proton.

Depending on the case, this nucleus is made up of:

- 1 proton and no neutron $_1^1H$
- 1 proton and 1 neutron $_1^2H$
- 1 proton and 2 neutrons $_1^3H$

I.5.3. Molecules

A molecule is an electrically neutral entity consisting of more than one atom **(** e.g. H2O Figure I.8). In another way, a molecule is a group of atoms bonded together so that they behave as a single particle. The noble gases (helium, neon, argon) behave like molecules.

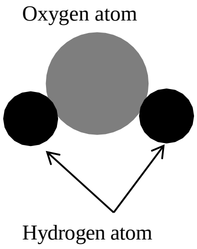


Figure 1.8: A representation of the water molecule

Since molecules are made up of atoms, chemists represent them by a formula $C_x H_y O_z \ldots$ which indicates: the nature of the atoms (C, H and O) and the number of atoms of each species represented by indices (x, y and z).

For example

- A hydrogen chloride molecule is composed of one hydrogen atom and one chlorine atom, so its formula is HCl .
- the water molecule, shown above, is composed of two hydrogen atoms (index 2) and one oxygen atom (index 1 is not written), its formula is H2O

To represent a molecule (compound) we use three ways:

- **The empirical formula** : indicates the proportions of atoms of the different elements present in the molecule. CH_2O is the empirical formula of glucose (molecular formula: $C_6H_{12}O_6$).
- **The molecular formula:** is in agreement with the molecular molar mass of the compound. It provides information on the nature of the elements and the number of each atom present in the molecule, for example ethane: C2H6 and Butane: C4H10
- **The structural formula**: provides more detail than the previous formulas. It represents the nature of the atoms, their bonds and their spatial arrangement.

1.6. Atomic and molecular units of measurement

I.6.1. Number of moles (n)

The mole (symbol: mol) is a base unit of the International System, adopted in 1971, which is mainly used in physics and chemistry. **The mole is the amount of substance in a system containing as many elementary entities as there are atoms in 12 grams of carbon 12 ($N_A = 6.023\ 10^{23}\ mol^{-1}$).**

The quantity of substance (number of moles) is a quantity for counting chemical or physical entities. The unit corresponding to it, in the international system, is the mole.

- *For a liquid or solid*

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

n: quantity of matter in mol

m: mass of the compound in g

M: molar mass of the compound in g mol $^{-1}$

Example

Calculate the number of moles of hydrated copper(II) sulfate ($CuSO4$, $5H2O$) contained in 5.00 g of this substance .

Solution

$M_{(CuSO4 \cdot 5H2O)}$ = (63.5 + 32 + 4 x 16 + 5 x 18) = 249.5 g/ mol

The amount of copper sulfate in moles.

$$n = \frac{m_{(CuSO4 \cdot 5H2O)}}{M_{(CuSO4 \cdot 5H2O)}} = \frac{5}{249,5} = 0,02 \text{ mol}$$

- *For a gas*

  The amount of matter is not equal

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

V: volume of gas in L (liters)

V_m : molar volume of the compound in L mol $^{-1}$

I.6.2. Atomic mass unit (amu)

An atomic mass unit is defined as the mass of 1/12 of a carbon-12 atom.

1 u = $1,661.10^{-27}$ kg

Example: m_e =0.000548 u, m_p =1.00728 u, m_n = 1.008 u

I.6.3 . Atom-gram, Molecule-gram

Mass (expressed in grams) of one mole of atoms of an element. The mole of hydrogen is equivalent to 2.016 g of hydrogen, that of oxygen to 32 g of oxygen, that of nitrogen to 28 g of nitrogen.

I.6.4. Molar mass (M)

Molar mass is the mass of one mole of a substance (a simple body, a chemical compound). It is expressed in grams per mole (g mol $^{-1}$ or g/mol).

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

M_H = 1.0 g.mol $^{-1}$; M_C = 12.0 g.mol $^{-1}$; M_O = 16.0 g.mol $^{-1}$.

Water has the chemical formula H2O, i.e. $M_{water} = 2 \cdot M_H + M_O = 2\times1 + 16 = 18$ g.mol $^{-1}$.

The molecular formula of methane is CH4, its molar mass = 12 + 4x1 = 16 g mol $^{-1}$

In 16g of methane there is one mole of methane and 16g of methane contains 6.022 x 10 ^{23} molecules of methane.

Application exercises

Exercises 1

We weigh 5.0 g of silver, whose molar mass is equal to 107.9 g.mol $^{-1}$.

1-Calculate the amount of silver matter in these 5.0 g.

2-Calculate the number of silver atoms present in these 5.0 g.

3-Deduce the mass of a silver atom.

4-Calculate the mass of a silver atom knowing that the silver studied is: 107(47)Ag . Compare this value with question 3-.

Given: m_{proton} = 1.67.10 $^{-27}$ kg (mass of electrons is negligible in this exercise and mass of a neutron = mass of a proton)

Solution

1-Quantity of silver : n = m / M. Numerical application: n = 5.0 / 107.9 = 4.6.10-2 mol.

2-Number of silver atoms:

In 1 mole of silver atoms there are: NA = 6.02.10 ^{23} silver atoms.

In n moles of silver atoms there are N silver atoms.

So: N = n . NA / 1 = 4.6.10- 2 . 6.02.1023 /1 = 2.77.1022 silver atoms.

3-Mass of a silver atom:

We know the molar mass of silver: M = 107.9 g.mol $^{-1}$

So: In 107.9 g of silver there are 6.02.10 ^{23} atoms of silver.

In m $_{atom}$ g of silver there is 1 atom of silver.

So: m $_{atom}$ = 107.9/6.02.10 ^{23} = 1.79.10-22 g = 1.79.10 $^{-25}$ kg.

4-Mass of a silver atom from the number of nucleons:

according to the formula given for silver we know the number of nucleons: A = 107

gold m $_p$ = m $_N$ SO m $_{atom}$ = A mp = 107 . 1.67 .10 $^{-27}$ = 1.78.10 $^{-25}$ kg . The atomic masses found are the same.

Exercises 2

Calculate the molar mass of the following compounds: carbon dioxide, sucrose, ammonia, methane, hydrogen chloride, sulfur dioxide

Solution

Carbon dioxide: CO2 : M = MC $_+$ 2MO $_=$ 12 + 32 = 44 g.mol $^{-1}$

Sucrose : $C_{12}H_{22}O_{11}$:M = 12 M $_C$ + 22 M $_H$ + 11 M $_O$ = 12.12 + 22.1 + 11.16 = 342 g.mol $^{-1}$

Ammonia: NH_3 : M = M $_N$ + 3.M $_H$ = 14 + 3 = 17 g.mol $^{-1}$

Methane: CH_4 : M = M $_C$ + 4 M $_H$ = 12 + 4.1 = 16 g.mol $^{-1}$

Sulfur dioxide: SO_2 : M = 32 + 2.16 = 64 g.mol $^{-1}$

Hydrogen chloride: HCl : M = M $_H$ + M $_{Cl}$ = 1 + 35.5 = 36.6 g.mol $^{-1}$

I.7. Chemical proportions in compounds

In order to determine any formula one must know how to calculate the percentage of each element in the compound. **In a chemical compound, the elements that compose it are always present in the same mass ratio** . The percentage of composition can be calculated according to the following formula:

$$x(\%) = \frac{m_x}{m_T} \times 100$$

Example 1

Calculate the mass percentage of nitrogen in ammonium nitrate NH_4NO_3

m(N) = 14 u we have two nitrogen atoms => m(N) = 28

m(NH_4NO_3) = 14 + 4 x 1 + 14 + 16 x 3 = 80 u

$$N(\%) = \frac{m_N}{m_T} \times 100$$

$$N(\%) = \frac{28}{80} \times 100 = 35\%$$

I.7.1. The simplest (empirical) formula

Just as mass percentage can be calculated from the chemical formula of a compound, the empirical formula can be calculated conversely.

Example

Find the empirical formula of a compound containing by mass: 27.3% carbon and 72.7% oxygen.

Solution

Symbol of the elements involved	C	O
Composition percentage	27.3	72.7
Denominated by atomic mass	$\frac{27,3}{12}$	$\frac{72,7}{16}$
The atomic ratio	2.3	4.5

The simplest integer ratio is that which is divided by the smallest whole number.

	$\frac{2,3}{2,3}$	$\frac{4,5}{2,3}$
It's approximately	1	2

The simplest formula is CO_2

I.7.2. The molecular formula

In order to find the molecular formula, we need the molecular mass as well as the empirical formula.

Example

Dichloromethane has a molecular mass of 99 u. Analysis of a sample shows that it contains 24.3% carbon, 4.1% hydrogen and 71.6% chlorine. What is its molecular formula?

Solution

Symbol of the elements involved	C	H	Cl
Composition percentage	24.3	4.1	71.6
Mass-denominated	$\frac{24,3}{12}$	$\frac{4,1}{1}$	$\frac{71,6}{35,5}$
The atomic ratio	2	4	2
The simplest ratio of the whole number	1	2	1

The simplest formula is CH_2Cl

The molecular mass of CH_2Cl = 12 + 2x1 + 35.5 = 49.5 u is not the molecular mass of dichloromethane which is 99 u. By multiplying the number of the three atoms by two we will have:

12x2 + 2x1x2 + 35.5x2 = 99u.

So the molecular formula of dichloromethane is $C_2H_4Cl_2$

I.8. Law of mass and conservation of mass (Lavoisier)

In the eighteenth century, chemical reactions were still somewhat of a mystery. Antoine Laurent Lavoisier (1743-1794), established an important principle based on chemical reactions. He stated that **the total mass of the products of the reaction is equal to the total mass of the reactants** . This statement is called the law of conservation of mass. This principle is illustrated by the following chemical reaction:

$$Ag^+ + Cl^- \rightarrow AgCl$$

Let there be an Ag $^{+}$ ion and a Cl^{-} ion , at the end of the reaction, the two ions have not disappeared, no new ones have appeared, they have simply chemically associated. If the sum of the mass of the reactants consumed during the reaction is 10 g, then the sum of the mass of the products formed at the end of the reaction is also 10 g.

I.9. Solutions

A solution is a mixture of two (or more) substances, it consists of a solvent which is usually present in large quantity and a solute (solid, liquid or gas) which is usually present in a smaller quantity. The amount of solute dissolved in a particular volume of solvent is called its concentration. Therefore, a **dilute solution** contains a low concentration of solute and a **concentrated solution** contains a high concentration of solute (Figure 1.9).

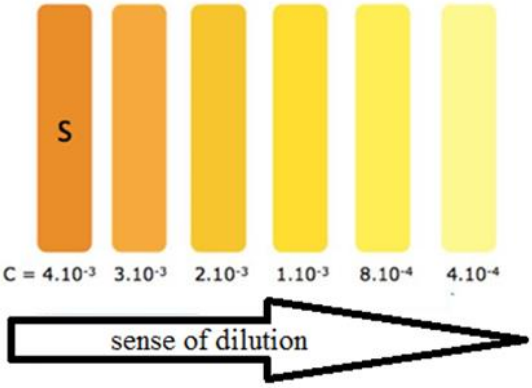


Figure 1.9: A representative diagram of degradation in concentration or dilution

I.9.1. dissolution

When a solution is prepared, the bonds between the solute particles are broken, and they spread throughout the solvent. This is called **dissolution.** New bonds are formed between the solute and the solvent molecules.

Example: H2O and NaOH (s) gives Na $^{+}$ (liq) + OH $^{-}$ (liq), by adding HCl we form NaCl .

I.9.2. Saturation

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

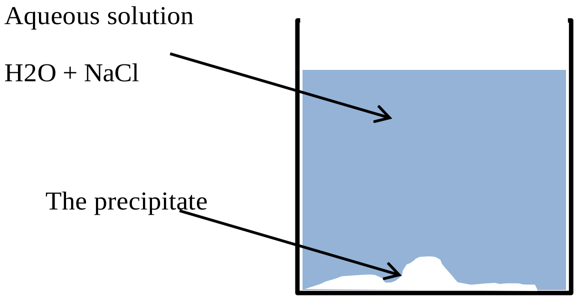


Figure I.10: A figure showing the NaCl precipitate

1.10. Concentration measurement laws

I.10.1. Molar concentration (Molarity)

The molar concentration, or molarity, or sometimes molar ratio of a chemical species, is the quantity of matter, expressed in moles per unit volume (1); this notion is essentially used for species in solution. The molar concentration of a species X is noted c $_X$ or [X].

$$c_x = \frac{number\ of\ solute\ moles}{volume\ of\ solution} = \frac{n}{V}$$

Example

90 g of glucose (C6H12O6) are dissolved in 1 liter of water. What is the molarity?

Solution

M($C_6H_{12}O_6$) = (6 x 12 + 12 + 6 x 16) = 180 g/mol.

$$\text{number of moles of glucose} = \frac{\mathrm{m}_{(C6H12O6)}}{\mathrm{M}_{(C6H12O6)}} = \frac{90}{180} = 0{,}5 \text{ mol}$$

$$the\ molarity\ (c_x) = \frac{n}{V} = \frac{0{,}5}{1} = 0{,}5\frac{mol}{l}\ ou\ 0{,}5\ M.$$

I.10.2. Molar volume

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

The molar volume can be determined for any substance in all phases (gas, liquid, solid). In the units of the International System, the molar volume is expressed in cubic meters per mole ($m^3 \cdot mol^{-1}$)

The molar volume is noted $\bar{V}$or V_m, it is worth:

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

V: the volume in cubic meters or liters;

n : the amount of matter in moles.

In the case of ideal gases; it is the volume occupied by one mole of substance in the gaseous state. Under normal conditions of pressure and temperature (P= 1Atm, T=0°C=273K), one mole of gaseous substance occupies a volume of 22.4L.

PV =n RT

P: pressure;

T: temperature;

A: the ideal gas constant.

Example

What volume of carbon dioxide can be obtained by the decomposition of 50 g of calcium carbonate under standard conditions of pressure and temperature (0°C and 1atm)?

Solution

We write the equilibrium equation of the reaction:

$CaCO3(s) \rightarrow CaO\ (s) + CO2(\ g)$

First we calculate the number of moles of CaCO3 involved in this reaction:

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

$m_{CaCO3} = 50g$ And $M_{CaCO3} = 40 + 12 + 16x3 = 100$ g/mol ⇒ $n = \frac{50}{100}$= 0.5 mol

We have 1 molecule of CaCO3 which gives 1 molecule of CO2

So 1 mol of CaCO3 gives 1 mol of CO2

SO 0.5 mol of CaCO3 induces 0.5 mol of CO2

We know that one mole of gaseous substance occupies a volume of 22.4L, that is to say that 0.5 mol of CO2 occupies a volume equal to 0.5 x 22.4 = 11.2 l.

I.10.3. Molality

Molality is the amount of substance, expressed in moles per unit mass (mol/kg).

$$\mathrm{b} = \frac{number\ of\ solute\ moles}{mass\ of\ solution} == \frac{\mathrm{n}}{\mathrm{m}}$$

Example

The molality of glucose in water (in the previous example):

$$\mathrm{b} = \frac{\mathrm{n}}{\mathrm{m}} = \frac{0{,}5}{1} = 0{,}5\ \mathrm{mol/kg}$$

I.10.4. Concentration and weight fraction

- The mass concentration of a solution corresponds to the mass of solute (g) dissolved or diluted in 1 L of solvent. This quantity is used for mixtures.

$$Cp = \frac{m_i}{V_{sol}}$$

Example

$_6H_{12}O_{6\,)}$ is dissolved in 1 liter of water. What is the mass concentration **?**

$$\left(\mathrm{m}_{(\mathrm{C6H12O6})}\right) = \mathrm{n}_{(\mathrm{C6H12O6})} \times \mathrm{M}_{(\mathrm{C6H12O6})} = 0{,}02 \times 249{,}5 = 5\ \mathrm{g}$$

So the mass concentration is worth;

$$\mathrm{Cp} = \frac{5}{1} = 5\mathrm{g/l}$$

- The mass fraction w_i of component i is the ratio of the mass m_i of this component to the mass m_{tot} of the mixture.

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

The mass fraction is between 0 and 1, and the sum of the mass fractions is 1.

I.10.5. The molar fraction

The mole fraction x_i of a component i is equal to the ratio of the number of moles n_i of this component to the number of moles of total n_{tot} of the mixture, it is therefore a dimensionless quantity. The mole fraction is between 0 and 1, and the sum of the mole fractions is 1.

$$x_i = \frac{n_i}{n_{tot}}$$

Example

Calculate the mass and molar fraction of oxygen (0.5 mol) mixed with nitrogen (0.7 mol).

Solution

We first calculate the mass of oxygen and nitrogen:

$$m_{O2} = n_{O2} \times M_{O2} = 0{,}5 \times 32 = 16\ g$$

$$m_{N2} = n_{N2} \times M_{N2} = 0{,}7 \times 28 = 19{,}6\ g$$

The mass fraction of oxygen:$w_{O2} = \frac{m_{O2}}{m_{tot}}$

$$w_{O2} = \frac{16}{35{,}6}$$

The mass fraction of oxygen:$x_{O2} = \frac{0{,}5}{1{,}2} = 0{,}41$

I.10.6. Normality (N)

Normality is the number of equivalents (Z) of solute per liter of solution (mol/l), it describes only the moles of reactive species per liter of solution, it is always a multiple of molarity and it describes the molar equivalents of the reactants involved in chemical reactions.

Normality can be calculated by the following formula

$$C_n = M*Z$$

C_n : normality

M: molarity

Z: the number of protons or electrons exchanged in the reaction

Example 1

A solution of H2SO4 that is 0.1 molar (0.1 M) implies a normality equal to 0.2 N, because there are twice as many moles of H+ ions in solution as moles of H2SO4 introduced. A solution of HCl or NaOH has the same normality as its molarity:

$$H_2SO_4 \rightarrow 2H + SO_4^{2-}$$

$$NaOH \rightarrow H + OH^-$$

Example

In its oxidation reaction, permanganate (KMnO4) exchanges 5e, so if its molarity is 0.01 molar, its normality is therefore equal to 0.05 normal:

$$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$$

I.10.7. Volume mass(ρ)

Density is a physical quantity that characterizes the mass of a material per unit volume. (kg/cm ^{3}).

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

Example

The mass of mercury contained in 54 cm ^{3} of volume equals 0.7344 kg. What is the density of mercury?

Solution

By applying the relation ρ =m/V we obtain a density equal to 0.0136 kg/cm ^{3}.

I.10.8. Density

Solid – Liquid : The density of a solid or liquid body is the ratio of its density to the density of a body taken as a reference. For liquids and solids, the reference body is pure water at 4 °C.

$$d = \frac{\rho_{(s\ ou\ l)}}{\rho_{H2O}} = \frac{\frac{m}{v}}{\frac{m'}{v}} = \frac{m}{m'}$$

<u>Gas:</u> The density of a gas is the ratio of the density of that gas to the density of air under the same conditions of temperature and pressure.

$$d_{gaz} = \frac{\rho_{gaz}}{\rho_{air}} = \frac{M_{gaz}}{M_{air}} = \frac{M_{gaz}}{28}$$

Example

Knowing that air is composed of approximately 80% nitrogen and 20% oxygen, determine the molar mass of air.

Mayr$M_{air} = 0{,}8 * M_{N2} + 0{,}2 * M_{O2} = 28{,}8\ g/mol$

II. Main constituents of matter

II.1. Introduction

Three particles form the basis of all matter: the proton, the neutron, and the electron. These particles are defined by two criteria: their electric charge and their masses. Protons have a positive charge, electrons have a negative charge, neutrons do not carry an electric charge. Protons and neutrons have relatively equal masses and are 1850 times heavier than electrons.

II.2. Faraday's laws: relationship between matter and electricity

If a sufficient potential difference is applied between two electrodes immersed in an electrolytic solution (HCl), the passage of an electric current and simultaneously a series of chemical reactions are observed at the electrode-electrolyte contact surface (Figure II.1).

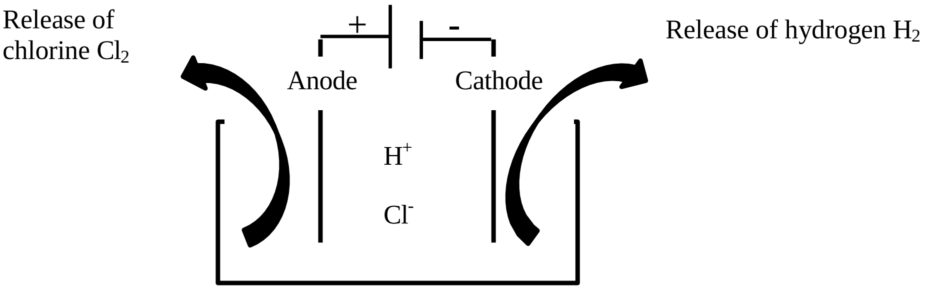


Figure II.1: Simplified diagram of the electrolysis of hydrochloric acid

At the electrodes, we see a release of gases in molecular form: a release of chlorine at the anode (+) and hydrogen at the cathode (-), this decomposition of hydrochloric acid is globally translated by the equation:

$$2HCl \longrightarrow H_2 + Cl_2$$

In solution, we know that HCl is dissociated into two ions H^+ and Cl^-. The fact that hydrogen appears at the negative electrode forces us to assume that the hydrogen ion is positively charged (Coulomb's law) and the chloride ion is negatively charged.

Faraday's First Law of Electrolysis:

The mass of the substance (m) deposited or liberated at any electrode is directly proportional to the quantity of electricity or charge (Q) passed.

Faraday's laws can be represented by the following form:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

m: the mass of the substance released at the electrode (g) and M its molar mass (g/mol)

Q: the total electric charge passed through the substance

F: Faraday's constant is 96485 C mol $^{-1}$,

Z: the valence of the substance

M/z corresponds to the equivalent of the total substance released.

II.3. Highlighting the constituents of matter

During the period 1875-1910, various experiments provided evidence that atoms are not the ultimate constituents of matter, and that they are themselves formed from several types of particles.

II.3.1. Highlighting electrons

When a strong potential difference (about 1000 V/cm) is established between two metal electrodes, in a glass tube containing a gas, and in which the pressure can be gradually reduced (Figure II.2), two phenomena are observed:

1) For a pressure of 0.1 to 0.01 atmosphere, luminescence is observed between the two electrodes.
2) For a pressure lower than 0.01 atmosphere the gas remains dark but the glass becomes fluorescent opposite the negative electrode (cathode). This fluorescence is due to the impact on the glass of invisible rays, coming from the cathode, which we call “cathode **rays”.**

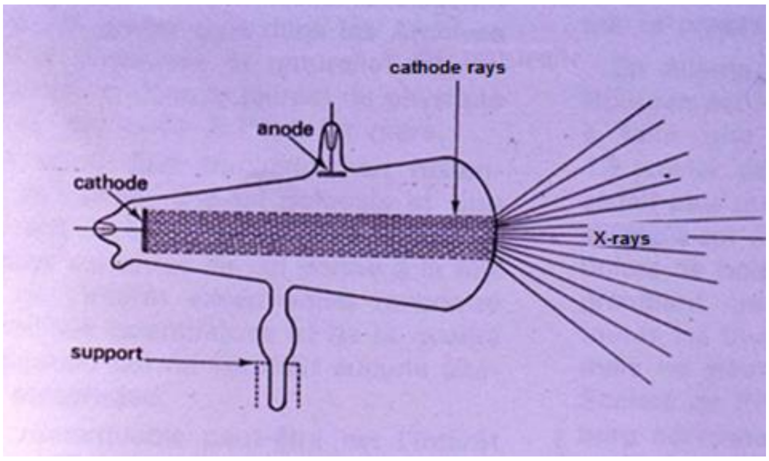


Figure II.2: Cathode ray experiment

II.3.1.1. Crookes experiments

In 1869, the British William Crookes developed the electron tube, called the Crookes tube, which consists of a glass bulb, in which a partial vacuum reigns, containing two electrodes. By applying a potential difference between the two electrodes, Crooks deduced that **the cathode rays move rectilinearly** (Figure II.3).

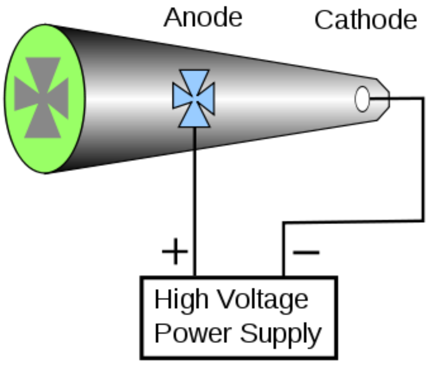


Figure II.3: Diagram of a Crookes tube

In 1895, Jean Perrin, observing the deflection of cathode rays in a Faraday cage, concluded that cathode rays are **negatively charged particles.**

II.3.1.2. JJ Thomson’s experiments

In 1897, Joseph-John Thomson was able to determine the charge-to-mass ratio (e/m) of cathode rays by measuring their deflection under an electric and magnetic field. He showed that this ratio is the same regardless of the gas in the bulb and the metal in the electrode. These particles, **called electrons** , are the universal constituents of matter.

a) Deflection under an electric field

Thomson designs a device in which an electron beam is deflected as it passes between two plates where an electric field prevails. Measuring the deflection of the electron beam then allows him to determine the ratio e/m $_e$ (Figure II.4).

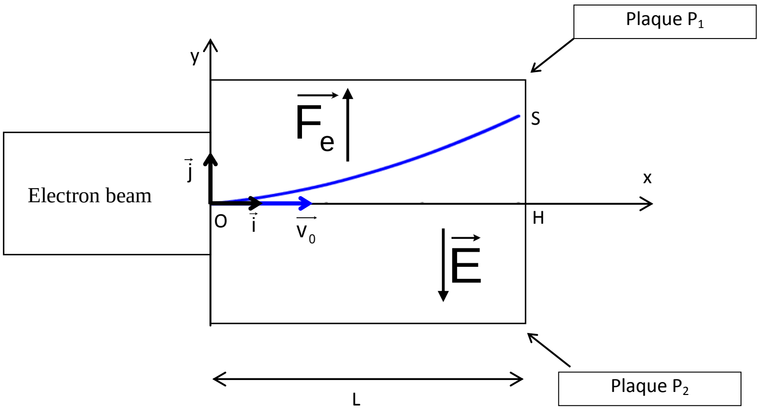


Figure II.4: Trajectory of the electron in a frame under an electric field

The trajectory of the electron is curved towards the plate P1 because of the effect of the electrostatic force $\vec{F}_e$. We deduce that this force has the direction towards the plate P1. It is indicated that the electric field $\vec{E}$ is perpendicular to the two plates and we know that $\vec{F}_e = -e.\vec{E}$. Thus the field $\vec{E}$ has a direction opposite to that of the force $\vec{F}_e$ and the force $\vec{F}_e$ is also vertical. Newton's second law is applied to the electron system, in the supposed Galilean terrestrial frame of reference.

$$\overrightarrow{\mathrm{F_e}} = \mathrm{m_e} * \vec{\mathrm{a}} = -\mathrm{e}\vec{\mathrm{E}} \; => \; \vec{\mathrm{a}} = \frac{-\mathrm{e} * \vec{\mathrm{E}}}{\mathrm{m_e}}$$

$\vec{a}$: The acceleration vector (direction opposite to the field vector $\vec{E}$)

By projection $\vec{a}\begin{cases} a_x = 0 \\ a_y = \dfrac{e.E}{m} \end{cases}$ As $\vec{a} = \dfrac{d\vec{v}}{dt}$, by integrating we obtain

$$\vec{v}\begin{cases} v_x = 0 + C_1 \\ v_y = \dfrac{e.E}{m_e}.t + C_2 \end{cases}$$

where C $_1$ and C $_2$ are constants integration that depend on the initial conditions.

At t = 0 $\overrightarrow{v_0}\begin{cases} v_{0x} = v_0 \\ v_{0y} = 0 \end{cases}$ => C1 = v $_0$ and C2 = 0.

SO $\vec{v}\begin{cases} v_x = v_0 \\ v_y = \dfrac{e.E}{m_e}.t \end{cases}$

We have $\vec{a} = \overrightarrow{a_x} + \overrightarrow{a_y}$

On the other hand $a_x = 0$ And $a_y = \frac{e*E}{m_e}$

This implies $a_y = \frac{d^2y}{dt^2}$

SO $\frac{d^2y}{dt^2} = \frac{e*E}{m_e}$

By integration $y = \frac{1}{2}\left(\frac{e*E}{m_e}\right)t^2$

In parallel $\frac{d^2x}{dt^2} = 0 \Longrightarrow \frac{dx}{dt} = v = v_0$

by integration $x = v_0 * t \Rightarrow t = \frac{x}{v_0}$

Replacing (t) with its value in y we will have:

$$y = \frac{1}{2}\left(\frac{e * E}{m_e}\right) * \frac{x^2}{v_0^2}$$

y : the apparent deviation

e : the charge of the electron (C)

m_e : the mass of the electron (kg)

E: the value of the electric field Vm^{-1}

x, D, L: the length of the plates

V_0 : initial speed of the electron

The recommended value of the e/m ratio determined by JJ Thomson is $1.75x10^{11}$ $C.kg^{-1}$, this discovery allowed him to have a Nobel prize in 1906.

Example

At the exit from the zone between plates P1 and P2 (Figure II.4), the electron has undergone a vertical deflection SY. Determine the value of the ratio (e/m_e).

We give y=YS = $2.0x10^{-2}$ m.

Length of plates: L = $9.0x10^{-2}$ m

Initial speed of the electron: $v_0 = 2.4x1^{07}$ ms^{-1}

Value of the electric field: E = $1.6x1^{04}$ Vm^{-1}

Solution

$$\frac{e}{m_e} = \frac{2 * y * v_0^2}{E * x^2}$$

The digital application gives

$$\frac{e}{m_e} = \frac{2 * 2 \times 10^{-2} \times (2{,}4 \times 10^{7})^2}{1{,}6 \times 10^{4} \times (9 \times 10^{-2})^2} = 1{,}8 \times 10^{11} C.kg$$

b) Deflection under a magnetic field

The deflection of a charged particle, such as an electron, under the influence of a magnetic field can be analyzed using the **Lorentz force**. Here's a step-by-step explanation:

An electron moving in a magnetic induction field $\vec{B}$ is subject to a magnetic force: $\overrightarrow{F_m} = -e * (\vec{v} \wedge \vec{B})$.

The negative sign indicates that the force on the electron is in the opposite direction to that of a positively charged particle moving in the same magnetic field.

Standard

In a magnetic field, the electron moves in a circular trajectory, and the magnetic force provides the necessary centripetal force. Using −e for the electron's charge, the equation becomes:

$$f_m = |qvB \sin \alpha|$$

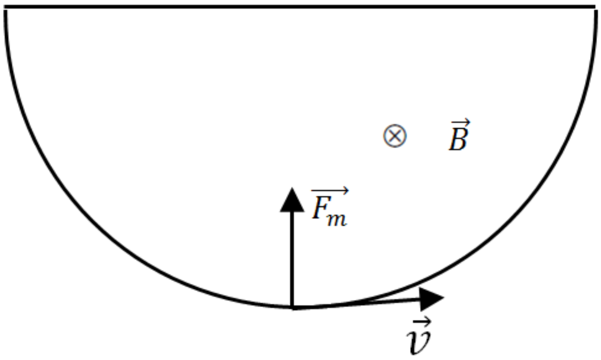


Figure II.5: Trajectory of the electron in a frame under a magnetic field

$F_m = q * v * B$(because sin 90 = 1)

$\sum F = m * \vec{a}$ => $m * a = e * v * B$

In a circular trajectory $a = \frac{v^2}{r}$ $\Longrightarrow$ $\frac{e}{m} = \frac{v}{B*r}$

r: the radius of the trajectory (m)

B: the value of the magnetic field (Tesla)

If we combine the two fields (magnetic and electric) so that they are equal and opposite, that is, their strengths are equal. At this moment, the beam is straight.

$\overrightarrow{F_e} = \overrightarrow{F_m}$ then $\quad e * v * B = e * E \Longrightarrow v = \frac{E}{B}$

we replace v by its value in y

The e/m ratio will be equal to: $\quad \frac{e}{m} = \frac{2*y*E}{B^2x^2}$

Example

Consider an electron moving in a magnetic field BBB and an electric field EEE. The electron is observed to be deflected by a distance yyy after traveling a distance xxx under the combined influence of these fields. The equation that relates these parameters is given by $\frac{e}{m} = \frac{2*y*E}{B^2x^2}$:

Given:

- y=2.0
- x=5.0 cm
- E=100 V/m
- B=0.01 T

Solution

$\frac{e}{m} = 6\ 10^6$ C/kg

II.3.1.3. Millikan's experiment

In this experiment, the quantum nature of the charge is experimentally determined. Robert Millikan received the Nobel Prize in Physics in 1923 for this brilliant experiment. A simplistic diagram of his apparatus is shown below. (Figure II.6).

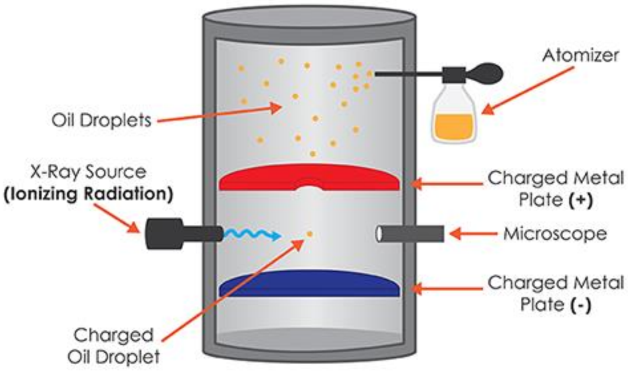


Figure II.6: Millikan's oil drop experiment

A spherical drop of oil, falling through a viscous medium like air, will quickly reach a constant velocity. When it reaches this equilibrium state, the viscous force is balanced by other forces acting on the fall, such as gravity, buoyancy of air, electrical forces, etc. In this experiment, through an ionization source an electrical force is introduced to modify the motion of the drop. By measuring the velocity of the oil drop under different conditions, the amount of charge can be determined. If the charge of the drop is an integer multiple of the fundamental unit (electron charge), one will be able to confirm the amount of charge.

a) In the absence of Rx

A droplet is subject to only two forces: gravity p and the Archimedes' thrust p' (Figure II.7). During its movement, the Stocks friction force f intervenes.

$p = mg = 4/3\ \pi\ r^3\ \rho\ g$ (ρ is the density of the oil , m the mass of the droplet)

$p' = m' g = 4/3\ \pi\ r^3\ \rho°g$ (ρ° is the density of air, the mass of air replaced by the droplet)

r is the radius of the droplet and g is the acceleration of gravity.

$f = 6\pi\ ŋ\ rv$ (ŋ is the viscosity of the air and v is the falling speed (in m/s))

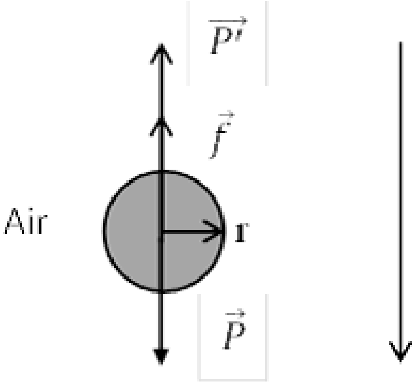


Figure II.7: Displacement of the oil drop under the effect of gravity and the force of Stocks.

Let us consider the balance of forces, taking the maximum value as the speed of movement (v).

$p + p' + f = ma = 0$ (a is the acceleration)

v (taken as a constant value)

$a = dv/ dt = 0$

after screening

$p- p' – f = 0.$

$p - p' = f$

$4/3 \pi r^3 (\rho - \rho°) g = 6 \pi ŋ rv$

$r^2 = 9 ŋ v / 2 (\rho - \rho°)g$

If we neglect the Archimedes thrust, the radius of the droplet has the expression:

$$r^2 = 9 ŋ v / 2 \rho g$$

b) In the presence of Rx

By applying a vertical (uniform) rectilinear electric field, the droplets will move towards the positive pole. By playing on the intensity of the field, we can then practically immobilize them.

The forces acting on an oil droplet in equilibrium:

Force due to gravitation ($\vec{p}$)

Force due to electric field$\vec{f_e}$

By immobilizing the drop, Stock force and force due to Archimedes' thrust =0

Force due to Archimedes' thrust$\overrightarrow{P'}$

$\vec{p} = mg = V * \rho * \vec{g} = 4/3 \pi * r^3 * \rho * \vec{g}$

$\vec{f_e} = q\vec{E}$

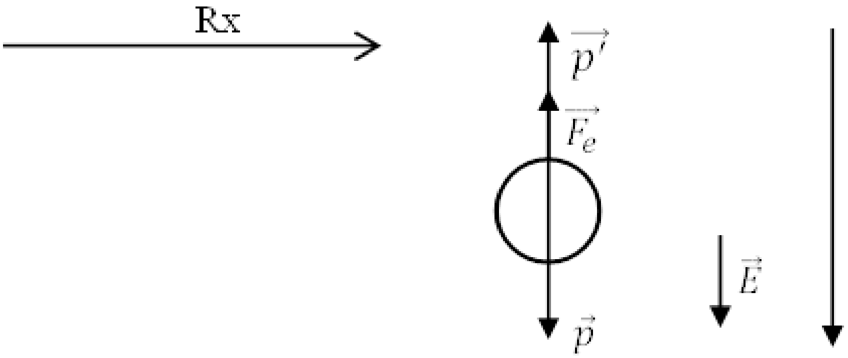


Figure 2.8: Displacement of the oil drop in the presence of X-rays

After projection, the balance of forces is written:

$p = f_e \Rightarrow$

$4/3 \pi * r^3 * \rho * g = qE$

$q = 4/3 \pi * r^3 * g * \rho / E$

The charge taken by the particles q is found to be a multiple of 1.602×10^{-19} coulomb, considered as the elementary charge. Depending on the volume of the drop q can be equal to 2e, 3e, 4e.

II.3.2. Highlighting the nucleus and its constituents

The discovery of the electron, a negatively charged particle, led to two questions: where does the mass of the atom reside? What is the counterpart of the negative charge of electrons, since the atom is neutral?

II.3.2.1. Rutherford experiment (demonstration of the nucleus)

Rutherford conducted a groundbreaking experiment to investigate the structure of the atom. He directed a beam of alpha particles, emitted from a radioactive source like polonium, onto a thin sheet of gold foil. By observing the deflection patterns of the alpha particles, he made a significant discovery (figure II.9).

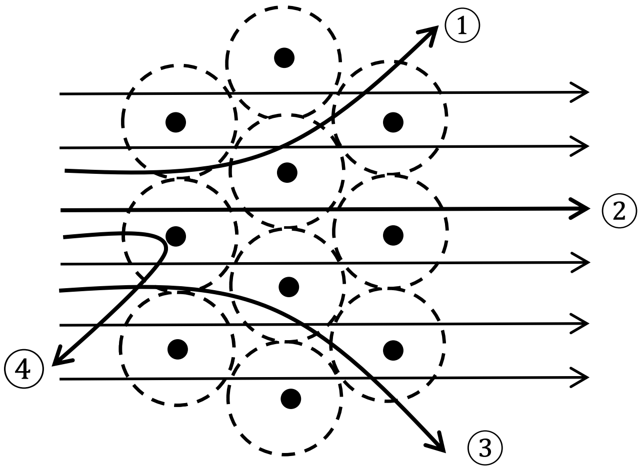


Figure II.9: Rutherford's experiment (1911)

He notes that most of the particles pass through the sheet without encountering any matter: the matter is therefore essentially made up of empty space. However, some of these particles are strongly deflected (Figure II.9).

Rutherford deduced that in matter (in this case in gold leaf) the mass is concentrated in particles, very dense and very distant from each other in relation to their dimensions, and positively charged at the center of the atom: the nuclei of the atoms.

II.3.2.2. Eugene Goldstein's experiment (demonstration of the proton)

In 1886, Eugène Goldstein (1850-1930) became interested in radiation similar to that of electrons observed in a vacuum tube. With equipment similar to that shown in the figure below, he studied the radiation having passed through a cathode pierced with holes (Figure II.10). He noticed that rays passed through the holes and headed in the opposite direction to the cathode rays. He called them **channel rays** , because they passed through the holes as if through channels.

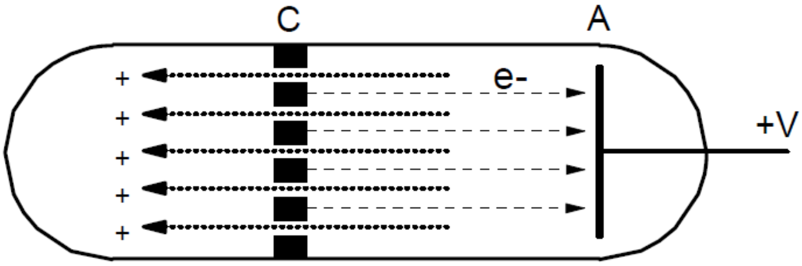


Figure II.10: Schematic of a canal ray tube, showing the rays exiting to the left of the perforated cathode.

Jean Perrin suggested in 1895 that they are made up of positively charged corpuscles. This suggestion was later confirmed, because these rays can be deflected by a magnetic field.

In 1914, Rutherford established that the hydrogen ion is the hydrogen atom without its electron and concluded that the hydrogen nucleus is a fundamental particle of every atomic nucleus. Rutherford would later call it the proton.

In 1919 Rutherford succeeded in the first nuclear reaction, by bombarding nitrogen with α particle. He noticed the emission of a positively charged particle, called a proton.

$$^{14}_{7}N + \propto \rightarrow \; ^{1}_{1}H + \; ^{17}_{8}O$$

This reaction shows that the proton is a constituent of the nitrogen atom. Characterization studies show that the proton is a particle with elementary charge +e and mass m_p .

$+e = +1,602.10^{-19}$ coulomb

$m_p = 1.67265 \times 10^{-27}$ kg.

= 1.0073 uma

II.3.2.3. Chadwick experiment 1932 (detection of the neutron)

Rutherford’s discovery led to research into other types of transmutation. Research focused on light nuclei since they were less likely to repel α particles . Thus, W. Bothe and H. Becker (1930) discovered extremely penetrating radiation from beryllium ${}_{4}^{9}Be$.

In 1932 Chadwick showed that this radiation must be composed of neutral particles of mass similar to that of the proton. The action of α particles on beryllium leads to the formation of the carbon 12 nucleus and emits "ultra-penetrating" rays (the neutron).

$$ {}_{4}^{9}Be + \propto \rightarrow {}_{6}^{12}C + {}_{0}^{1}n $$

It was he who even declared that these particles had the same mass as a proton but that the charge of these particles was zero ($m_n = 1.67495 \times 10^{-27}$ kg = 1.0087 amu)

II.4. Rutherford's planetary model

The ancient Greeks were interested in the nature of matter. **Empedocles of Agrigento (c. 5th century BC)** claimed that matter was composed of four elements: water, air, earth, and fire. **Democritus (460–370 BC)** claimed that matter was made up of small particles that he called atomos (indivisible in ancient Greek). In contrast, Aristotle (384–322 BC) claimed that matter was infinitely divisible. For philosophical reasons, Aristotle's theory dominated until the 19th century.

Air analyses have allowed **Dalton (1808)** to develop a model of the atom:

- Each element is made up of indivisible particles: atoms.
- Atoms of an element all have the same mass. Atoms of different elements are distinguished by their mass.
- Atoms can neither be destroyed nor produced by chemical reactions.

- In chemical reactions, atoms of different elements bond in a specific ratio.

Thomson (1897) imagines the atom as a sphere filled with an electrically positive substance and stuffed with negative electrons like raisins in a cake.

The model established by **Rutherford (1911)** was completed by Chadwick after the discovery of the neutron (1932). It is stated as follows:

1. Atoms are made up of electrons orbiting the nucleus of the atom. Electrons are negatively charged. By agreement, electrons are assigned a charge of -1. The circular paths of electrons are called shells or orbits. The radius of an atom is equal to the radius of the outermost electron orbit.
2. The nucleus is made up of two types of particles, protons (which have a relative charge of +1) and neutrons (which have a mass roughly equal to that of the proton but no electric charge). Protons and neutrons are collectively called nucleons.
3. Protons and neutrons are much heavier than electrons. This means that most of the mass of an atom resides in its nucleus. The number of protons added to the number of neutrons is called the mass number (symbolized A) of the atom.
4. The atom is made up of a large empty space.
5. Atoms are electrically neutral. This is because the number of protons and electrons is equal. The number of protons in an atom is called its atomic number (symbolized Z).
6. The atoms of each element are different because they have different numbers of protons (i.e. different atomic numbers). The helium atom consists of a nucleus of two protons and two neutrons surrounded by two electrons, so we can write Z= 2 and A= 4

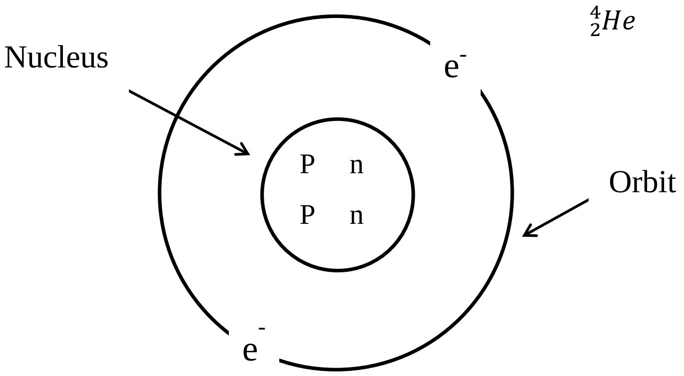


Figure II.11: Representation of the helium atom according to the Rutherford model. p: proton, n: neutron and e: electron

The helium atom is symbolized by ^4_2He. This symbol is constructed as follows:

- He is the chemical symbol for helium
- The number 4 indicates the atomic mass of helium
- The number 2 indicates the atomic number of helium

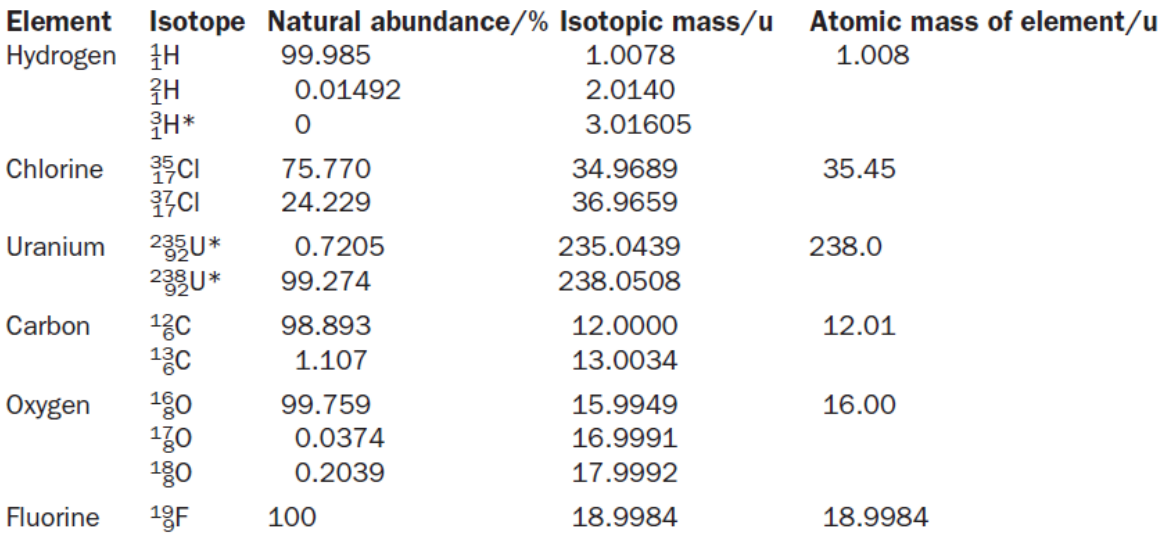
II.5. Isotopes

Atoms that are equal in number of protons but different in number of neutrons are called isotopes. In other words: isotopes are elements that have the same atomic number but different in mass number. For example, we have the following two isotopes of carbon : $^{12}_6C$, $^{13}_6C$. Both isotopes contain 6 protons and 6 electrons but 6 neutrons for $^{12}_6C$and 7 neutrons for $^{13}_6C$and the latter is heavier because it contains one more neutron.

II.5.1. Isotopic abundance

The natural abundance of each isotope is defined as the atomic percentage of that isotope in the sample. Currently the natural abundance of isotopes is now known (Table II.1).

Table II.1: Isotopic and atomic data for some chemical elements



Element	Isotope	Natural abundance/%	Isotopic mass/u	Atomic mass of element/u
Hydrogen	$^1_1$H	99.985	1.0078	1.008
	$^2_1$H	0.01492	2.0140	
	$^3_1$H*	0	3.01605	
Chlorine	$^{35}_{17}$Cl	75.770	34.9689	35.45
	$^{37}_{17}$Cl	24.229	36.9659	
Uranium	$^{235}_{92}$U*	0.7205	235.0439	238.0
	$^{238}_{92}$U*	99.274	238.0508	
Carbon	$^{12}_6$C	98.893	12.0000	12.01
	$^{13}_6$C	1.107	13.0034	
Oxygen	$^{16}_8$O	99.759	15.9949	16.00
	$^{17}_8$O	0.0374	16.9991	
	$^{18}_8$O	0.2039	17.9992	
Fluorine	$^{19}_9$F	100	18.9984	18.9984

Isotopes of the same element perform the same chemical reactions, although they have slightly different physical properties (such as boiling point, or density). For example, hydrogen gas is composed of normal hydrogen $^1_1H_2$and hydrogen gas is composed of deuterium$^2_1H_2$ undergo the same chemical reactions. Their combustion leads to the formation of normal water$^1_1H_2O$ and heavy water $^2_1H_2O$respectively. The boiling point and density are greater in $^2_1H_2$than in $^1_1H_2$and they are greater in $^2_1H_2O$than in $^1_1H_2O$.

II.5.2. Determination of isotopic abundance

Some molecules are in fact made from deuterium (D or $^2_1H_2$) in a proportion of 0.015%: this percentage represents the isotopic abundance of deuterium in water.

$$x_i\ (\%) = \frac{number\ of\ atoms\ of\ a\ given\ isotope}{total\ number\ of\ atoms\ of\ all\ isotopes\ of\ this\ element} \times 100$$

II.5.3. Molar mass of the element

As an element is made up of a mixture of various isotopes and the proportions of these various isotopes are constant, we can define for each element an average molar mass which will take into account its composition:

$$M = \sum x_i \times M_i$$

x_i denoting the natural abundance of isotope i of molar mass M_i .

Example

Natural copper is composed of two stable isotopes with atomic masses of 62.929 (A1 = 63) and 64.927 (A2 = 65) respectively. The atomic number of copper is Z=29.

Indicate the composition of the two isotopes.

Knowing that the molar mass of the natural isotope mixture is 63.540, calculate the abundance of the two isotopes.

Cu: Z = 29

Isotope 1: M1 = 62.929 g mol-1 N1 = 34

29 protons; 29 electrons and 34 neutrons

Isotope 2: M2 = 64.927 g mol-1 N2 = 36

29 protons; 29 electrons and 36 neutrons

$$M = \sum x_i \times M_i$$

Mcu = x1 M1 + x2 M2

S xi = 1 => x1 + x2 = 1 Þ x2 = 1 - x1

Mcu = x1 M1 + (1 - x1) M2 = x1 M1 + M2 + x1 M2

Mcu - M2 = x1 (M1 - M2)

x1 = (Mcu - M2) / (M1 - M2) = (63.540 - 64.927) / (62.929 - 64.927) = 0.6942

$${}^{63}_{29}Cu = 69{,}42\%$$

$${}^{65}_{29}Cu = 30{,}58\%$$

II.6. Separation of isotopes (Bainbridge spectrometer 1933)

Method of characterizing matter which is based on the determination of the atomic or molecular masses of the individual species present in the sample (Figure II.12).

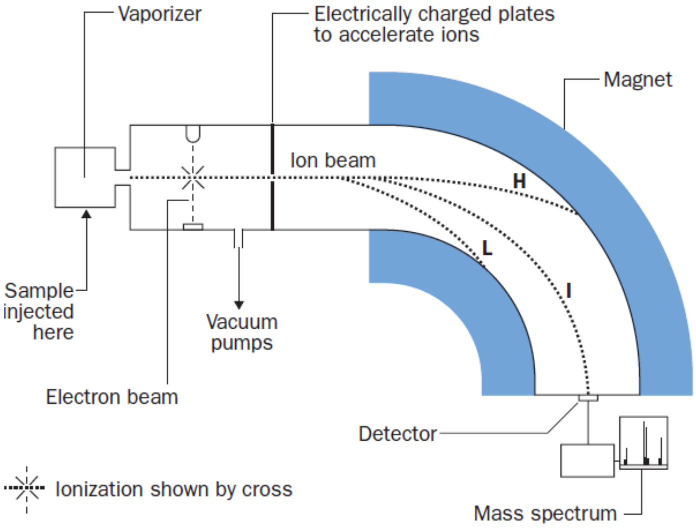


Figure II.12: Representative diagram of a mass spectrometer

A mass spectrometer causes atoms to ionize by losing electrons, in a process called ionization. The loss of an electron means that the atom is positively charged (positive ions).

Positive ions are separated in the mass spectrometer according to the mass-to-charge ratio m /e of the ion, e is the relative charge of the ion (e.g. e= 1 for O^{+1} and e= 2 for Cl^{+2}), and m is the mass of the ion in atomic mass units. Suppose that a mixture of neon gas (consisting of the isotope atoms neon-22, neon-21, and neon-20) has been injected into a mass spectrometer, the steps involved in the mass spectrometer are as follows:

Velocity filter: the ions (mass m and charge +q) are subjected to a uniform and perpendicular electric field E and magnetic field. The ions are subjected to the electric force Fe = qE and the magnetic force Fm = q (V ^ B). The beam deflection is zero if these forces compensate each other. The initial velocity V of the ions that can enter the analysis chamber is therefore equal to: V = E /B

Analyzer: The ions are then subjected to the action of a single magnetic field and describe in the analysis chamber (where a high vacuum reigns) a circular trajectory whose radius is given by the relation: R = mv/qB

If n is the number of nucleons (mass number) of the ion, its mass m is approximately equal to n.1.6710 -27 $^{\text{kg}}$. We only take into account ions with charge q = +1.6.10 $^{-19}$ C

Impact distance

The impact distance can be interpreted as the difference between the diameters of the trajectories followed by ions deflected by the same magnetic field, or as the separation of their points of impact on a detector.

In the magnetic field, the ions follow a circular trajectory with a radius riri such that:

$$r_i = \frac{m_i v}{q_B} \quad \text{et} \quad d = 2(r_2 - r_1)$$

$$d = 2\left[\frac{m_2 v}{qB} - \frac{m_1 v}{qB}\right] = \frac{v}{NA.q.B}(M_2 - M_1)$$

II.7. Nuclear energy

II.7.1. Mass and energy: Einstein's relationship

During a nuclear transformation (natural or induced), the mass of the products is always slightly less than the mass of the reactants. The loss of mass is noted Δm . Associated with this loss of mass, there is a release of energy whose value ΔE is given by the Einstein relation:

$$\Delta \text{E} = (\Delta \text{m}) c_0^2$$

where c_0 is the speed of light in vacuum.

II.7.2. Cohesive energy of a nucleus

The binding energy of a nucleus is the energy that must be supplied to the nucleus to dissociate it into its different nucleons. A nucleus is all the more stable as this quantity ΔE is large. This is why ΔE is called the cohesion energy (or binding energy) of the nucleus.

Precise measurements have shown that the mass of a particular atom is always slightly less than the sum of the individual masses of its components (neutrons , protons and electrons), this difference called the **mass defect (Δm).** The mass defect can be calculated using the following equation:

$$\Delta m = \left[Z * \left(m_p + m_e\right) + (A - Z) * m_n\right] - m_{\left({}_{Z}^{A}X\right)}$$

Δm : mass defect

Z: atomic number (number of protons)

A: atomic mass (number of nucleons)

m_p : proton mass

m_e : mass of the electron

m_n : neutron mass

$m_{\left({}_{Z}^{A}X\right)}$: mass of the atom

Exercise II.3

Calculate the mass defect of lithium-7 (${}_{3}^{7}Li$), let us know that its atomic mass is 7.016003 amu .

Proton mass = 1.00727 amu

Neutron mass = 1.00867 amu

Electron mass = 0.00054 amu

Solution

$\Delta m = \left[Z * \left(m_p + m_e\right) + (A - Z) * m_n\right] - m_{\left({}_{Z}^{A}X\right)}$

$\Delta m = [3 * (1{,}007826) + (7 - 3) * 1{,}00867] - 7{,}016003$

$\Delta m = 0{,}0421335\ uma$

Exercise II.4

Calculate the mass defect and binding energy for uranium-235. An atom of uranium-235 has a mass of 235.043924 amu .

Solution

Step 1: Applying the mass defect equation

we obtain $\Delta \mathrm{m} = 1,91517 \text{ uma}$

Step 2: Using the mass defect and Einstein's equation we can calculate the binding energy.

$$\Delta \mathrm{E} = (\Delta \mathrm{m}) c_0^2 = 1,91517 \times \underbrace{1.66054 \times 10^{-27} \times (2,9979 \times 10^8)^2}_{\text{This multiplication is constant}}$$

This multiplication is constant
$1,4923 \times 10^{-10}$ J = 931254168 eV= 931,2 MeV

$\Delta \mathrm{E} = \Delta \mathrm{m}(\mathrm{uma}) \times 931,2$

$\Delta \mathrm{E} = 1,91517 \times 931,2 = 1784 \text{ MeV}$

II.7.3. Binding energy per nucleon

It is equal to the binding energy of the nucleus divided by the number of nucleons (A) present in this nucleus:

$$\frac{E_L}{A}$$

Example

The binding energy per nucleon of a uranium-235 nucleus is:

$\frac{E_L}{A} = \frac{1784}{235}$= 7.59 MeV/ nucleon

II.7.4. Nucleus stability

II.7.4.1. Aston curve

Aston curve represents the graph associated with $-E_L/A = f(A)$. It allows to compare the stability of different atomic nuclei. A nucleus is all the more stable as its average energy per nucleon is high, the most stable nuclei are at the bottom of the graph. Light nuclei will evolve by fusion, while heavy nuclei will evolve by fission.

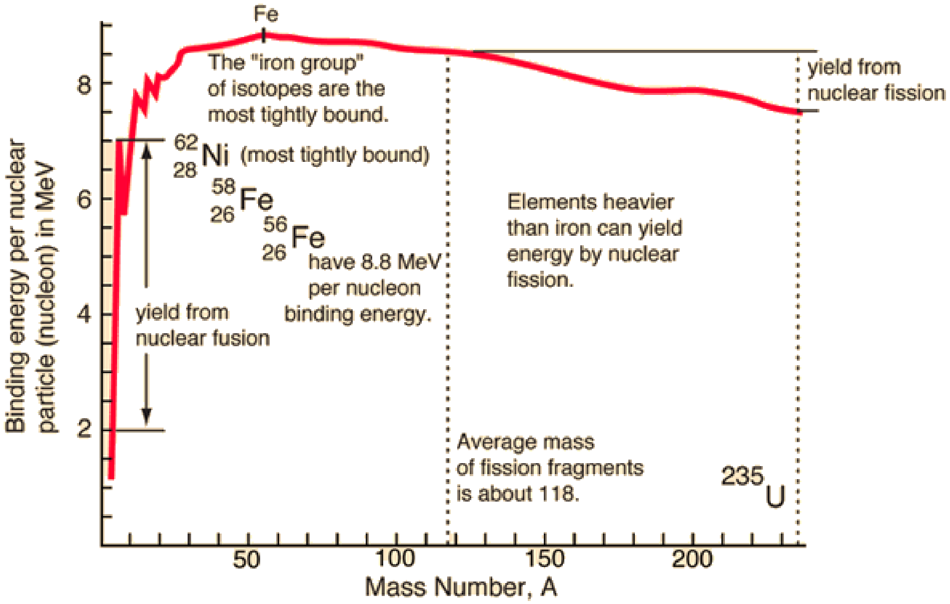


Figure II.16: Aston curve

Example

The binding energy of an oxygen 16 nucleus is 126 MeV, that of the uranium 238 nucleus is 1802 MeV.

To compare their stability it is necessary to calculate the binding energy per nucleon.

We find:

$(^{16}_{8}O) E_L/A = 126/16 = 7.88$ MeV/nucleon

$(^{238}_{92}U) E_L/A = 1802/238 = 7.57$ MeV/nucleon

The oxygen 16 nucleus is therefore more stable than the uranium 238 nucleus.

II.7.4.2. The Valley of Stability

The valley of stability refers to the place where the stable isotopes are located, when the atomic number is plotted on the abscissa and the number of neutrons of each isotope on the ordinate (map of nuclides), the two axes are sometimes reversed in certain representations.

If we draw a diagram, in which we represent the number of neutrons = f (Z: number of protons) (Figure II.16) we see that the stability of light elements is achieved when the number of neutrons and the number of protons are approximately equal (N = Z).

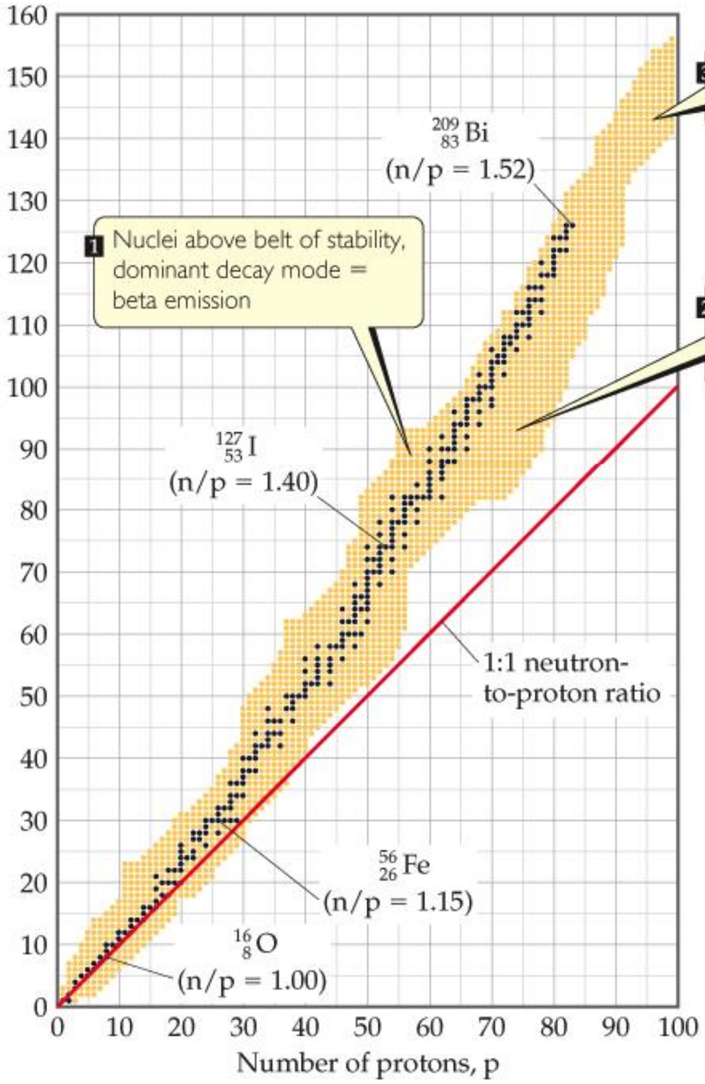


Figure II.17: Diagram of stable nuclides as a function of their numbers of protons (Z) and neutrons (N)

We distinguish 4 different areas:

- The black area represents the stable chemical elements (valley of stability). We note that for light nuclei (A < 20) the stable nuclei are on the bisector.

  Beyond (A > 20), stable nuclei deviate from this bisector. They need more neutrons than protons to remain stable.

- The blue area represents unstable nuclei with an excess of neutrons. These nuclei return to the stability line by β- decay .
- The orange area represents unstable nuclei with an excess of protons. These nuclei return to the stability line by β+ decay or by electron capture, which transforms a proton into a neutron within the nucleus.
- Heavy nuclei rich in protons return to the stability line by alpha decay.
- The yellow area represents unstable nuclei with excess mass that tend to undergo fission reactions.

III. Radioactivity

When a nucleus undergoes a transformation resulting in another nucleus emitting particles and sometimes electromagnetic radiation, this phenomenon is called "radioactivity".

Radioactivity was discovered by chance in 1896 by Antoine Henri Becquerel (1852-1908). While storing uranium salts with a blank photographic plate and after a few days, he noticed that this plate bore traces of radiation even though the salts had remained protected from light. Becquerel drew two conclusions from this:

- uranium naturally emits its own radiation,
- the intensity of this radiation persists over time.

He wonders where uranium can draw its energy with such persistence, Henri Becquerel has just **discovered radioactivity.**

Later, Marie Curie and her husband Pierre gave them the name radioactivity (from the Latin radius, ray). In 1898, the couple discovered two still unknown radioactive elements, polonium and radium. There are two types of radioactivity: natural and artificial.

III.1. Natural radioactivity

We speak of "natural radioactivity" to designate sources not produced by human activities, such as that from radon, the earth, or cosmic radiation. Currently the main natural radionuclides are potassium 40 and those from the three radioactive families of uranium 238, uranium 235 and thorium 232. These radioactive elements are found in the air, in the soil, in water and in living organisms including humans. The natural disintegration of a nuclide can be represented as follows: parent nuclide → daughter nuclide + nuclear radiation

where the term "nuclide" denotes an atom of a particular isotope.

III.2. Artificial radioactivity

Artificial radioactivity is the set of phenomena of transmutation of radioisotopes created artificially by bombarding stable elements (aluminium, beryllium, iodine, etc.) with various particle beams (neutron, proton, α particle, deuteron).

This radioactivity was discovered by Frédéric Joliot and Irène Joliot-Curie, in an experiment to produce phosphorus 30, by bombarding aluminium 27 with an α particle generally coming from a radium source.

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

A nuclear reaction is caused when a projectile nucleus strikes a target nucleus and gives rise to two new nuclei. An artificial nuclear reaction can be fusion or fission.

III.2.1. Nuclear fission reaction

It occurs when a slow neutron (Ec = 0.1 MeV), called a thermal neutron, encounters a fissile nucleus such as uranium 235; which causes the birth of two lighter nuclei.

$${}^{1}_{0}n + {}^{235}_{92}U \rightarrow {}^{94}_{38}Sr + {}^{140}_{54}Xe + 2{}^{1}_{0}n$$

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

The energy released is 200 Mev /atom. The fission of 1g of uranium is equivalent to the combustion of 3 tons of coal. A fission reaction will give rise to daughter nuclei but also to neutrons, these being able to meet other nuclei, we then obtain a chain reaction.

III.2.2. Nuclear fusion reaction

To have nuclear fusion, two light nuclei must unite to form a heavier nucleus.

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

These light nuclei are this time composed of neutrons and protons, so they need a very high energy to overcome the repulsive forces: The medium is then brought to a very high temperature (10^{8} K). Therefore, the fusion reaction is called a thermonuclear reaction . .

III.2.3. Mass and energy balance of a nuclear reaction

Let any nuclear reaction be given with the equation:

$$ {}^{A}_{Z}A + {}^{A}_{Z}B \longrightarrow {}^{A}_{Z}C + {}^{A}_{Z}D $$

There are two ways to calculate the energy released by nuclear transformation:

- Using **mass variation** :

$$ \Delta E = [(m(A) + m(B)) - (m(C) + m(D))] \times c^2 $$

- Using the **binding energies** of the nuclei and according to the definition of El:

$$ \Delta E = [E_l(A) + E_l(B)) - (E_l(C) + E_l(D)] $$

Example

1. Write the decay equation for radium ${}^{226}_{88}Ra$

2. Calculate the energy released during disintegration:

of a radium 226 nucleus (in MeV)

nucleus	**Mass (u)**
Radium	225,9770
Radon	221,9702
Helium	4,0015

$c = 2.9979 \times 10^{8}\ ms^{-1}$

1. Radium decay equation

$$ {}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + \alpha $$

2. Energy released:

$\Delta E = \Delta m * c^2 = (225.9770 - (4.0015 + 221.9702)) * 1.66054 * 10^{-27} * (2.9979 * 10^{8})^2$

$\Delta E = 0.0053 * 931.5 = 4.9369$ MeV

III.3. Nuclear radiation

Alpha, beta and gamma rays are helium nuclei, electrons (and positrons) and photons, respectively, emitted during the radioactive decay of radioactive nuclides. These radiations have different penetrating powers (Figure III.1).

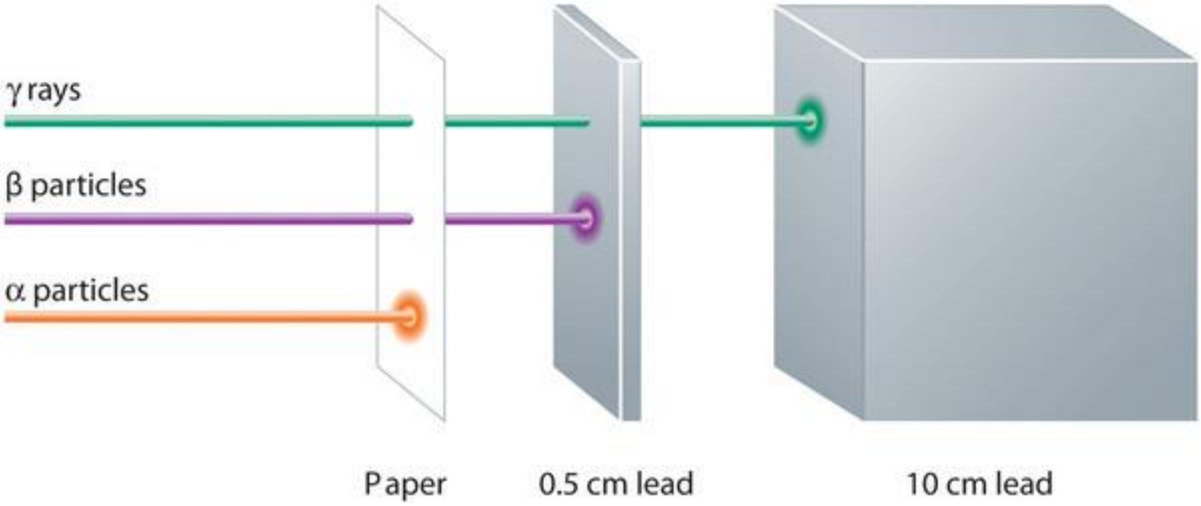


Figure III.1: Penetrating powers of nuclear radiation α, β, γ

III.3.1. Alpha rays (α)

This is a flow of helium nuclei ${}_{2}^{4}He^{+2}$ or ${}_{2}^{4}\propto$

Example $${}_{92}^{238}U \rightarrow {}_{90}^{234}Th + {}_{2}^{4}\propto$$

α particles only penetrate matter superficially (10 cm in air, 0.1 mm in water, 0.05 mm in Pb, the skin stops them).

A general rule: the radioactive element (X) transforms into another equally radioactive or stable element (Y) followed by the emission of a particle α:

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

III.3.2. Beta rays (β^{-})

These are electrons (β^{-1}, ${}_{-1}^{0}e$) resulting from the transformation of a neutron into a proton:

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

$${}_{90}^{234}Th \rightarrow {}_{91}^{234}Pa + {}_{-1}^{0}e$$

A general rule: the radioactive element (X) transforms into another equally radioactive or stable element (Y) followed by the emission of a particle β

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

β rays can pass through a thickness of 2 to 3 mm of aluminum.

III.3.3. Beta rays (${}_{1}^{0}e$ β^{+})

It only concerns artificial radioactive nuclei. It affects nuclei with too many protons compared to the number of neutrons. A proton from the parent nucleus transforms into a neutron by emitting a particle called a positron or positron (β^{+}).

$$ {}_{7}^{13}N \rightarrow {}_{6}^{13}C + {}_{1}^{0}e $$

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

III.3.4. Gamma rays (γ)

They are constituted by electromagnetic radiation, have an energy which varies from 0.01 to 10 MeV and they are very penetrating; they are stopped only by 10 cm of Pb. These radiations, come during a return to the stable (fundamental) state of a nucleus (de-excitation), therefore the emission of the rays γ does not change either A or Z.

$$ A^{*} \rightarrow A + \gamma $$

A^{*} excited nucleus

With de-excited nucleus

III.4. Radioactive families

The disintegration by steps α and β is done until a stable nucleus is obtained.

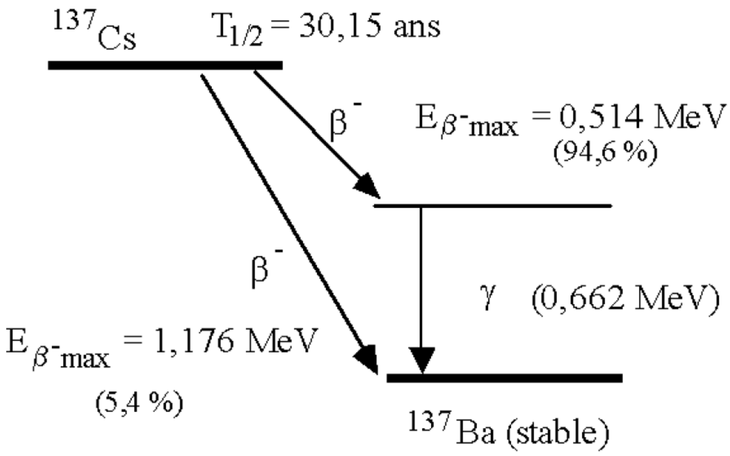


Schéma de désintégration du césium 137

It is a series or family of radioactive nuclides which are distinguished by the mass number:

- Uranium family A= 4n+2, where n is a natural integer . $^{238}_{92}U \rightarrow {}^{206}_{82}Pb$
- Actino-uranium family , A = 4n + 3 $^{235}_{92}U \rightarrow {}^{207}_{82}Pb$
- Thorium family, A = 4n $^{232}_{90}Th \rightarrow {}^{207}_{82}Pb$

In addition to the natural radioelements belonging to these three families, there are five other natural radioactive elements with a very long half-life: potassium 40, rubidium 87, samarium, lutetium, rhenium.

- **Isotopes**: These are atoms of the same element that have the **same number of protons** but **different numbers of neutrons**. This results in different atomic masses but identical chemical properties. For example:

  - Carbon-12 (6 protons, 6 neutrons)
  - Carbon-14 (6 protons, 8 neutrons)

- **Isotones**: These are atoms that have the **same number of neutrons** but **different numbers of protons**. Isotones belong to different elements but share similar nuclear properties. For example:

  - Carbon-14 (6 protons, 8 neutrons)
  - Nitrogen-15 (7 protons, 8 neutrons)

- **Isobars**: These are atoms that have the **same atomic mass** (or mass number, the sum of protons and neutrons) but **different numbers of protons and neutrons**. This means they are different elements but have the same overall mass number. For example:

  - Carbon-14 (6 protons, 8 neutrons)
  - Nitrogen-14 (7 protons, 7 neutrons)

Radioactive decay kinetics

III.5.1. Radioactive decay laws

Radioactive decay law describes the time evolution of the number of radioactive nuclei in a sample. The decay kinetics of a radioactive element (N) is a first-order process.

$$N \overset{\lambda}{\rightarrow} \mathrm{X}$$

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

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

we deduce, by integrating, the number N of radionuclides still existing at time t:

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

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

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

N_0: number of nuclei at t = 0

λ : decay constant (s^{-1}), it only depends on the nature of the radioactive nuclei and is independent of temperature.

Since the number of atoms in a radionuclide is proportional to its mass, the N_t and N_0 can be replaced by the mass of the radionuclide at time t (symbolized by m_t) and t=0 (symbolized by m_0) respectively:

$$m(t) = m_0 e^{-\lambda t}$$

These equations show that the decrease in the number of radionuclide atoms with time is exponential. Indeed, any quantity that is proportional to the number of atoms can also be substituted into these equations.

III.5.2. Radioactive period

The period T (half-life time $t_{1/2}$) is the time after which the number of nuclei initially present has been divided by a factor of 2 (Figure III.2).

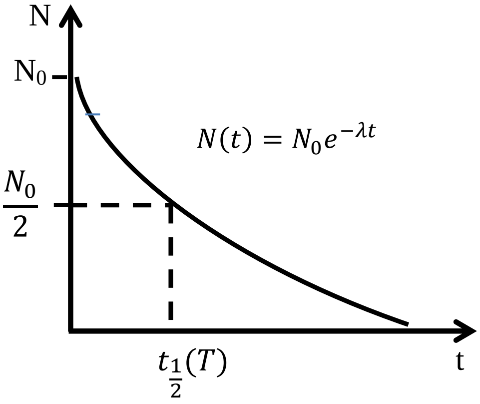


Figure III.2: Decay curve of a nuclide

We have

$N(T) = N_0 e^{-\lambda T}$ And $N(T) = \frac{N_0}{2} \Longrightarrow$

$\frac{N_0}{2} = N_0 e^{-\lambda T} \Longrightarrow \frac{1}{2} = e^{-\lambda T} \Longrightarrow$

$2 = e^{\lambda T} \Longrightarrow \lambda T = ln2 \Longrightarrow$

SO $$T = t_{\frac{1}{2}} = \frac{ln2}{\lambda}$$

Examples of period:

^{14}C: 5730 years

^{18}Ne: 1672 ms

^{235}U: 703.8 million years

III.5.3. Activity

Activity "A" is the fundamental quantity of radioactive decay, it means the number of decays per unit of time. The former unit of measurement is the curie (Ci), it was introduced in 1930, it corresponds to 3.7×10^{10} decays per second. Since 1975, the internationally recommended unit is the becquerel (Bq) defined as 1 decay per second (1 dps).

Activity, being the measure of the rate of decay, is related to the number of radioactive atoms N by the following expression:

$$A = -\frac{dN}{dt} = \lambda * N \qquad (1)$$

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

So (1) becomes $A(t) = \lambda * N_0 * e^{-\lambda t}$ (2)

In the initial state we write$A_0 = \lambda * N_0$

So relation (2) is written as follows:$A(t) = A_0 * e^{-\lambda t}$

Decay usually produces radiation particles (α , ß) or photons (γ) which can be detected with a certain probability. Under favorable conditions, the observed activity A'thus determined will be proportional to the actual activity (also called: absolute activity) A:

$$A' = A * \eta$$

Where η $(\leq 1)$is the detection efficiency ?

Example

1) Calculate the initial activity of a sample of radium 226 of mass m = 1.0 g. $\lambda = 4.3.10^{-4}$ year $^{-1}$

2) Calculate the activity of this sample 1000 years later.

Solution

1) Mass of a radium 226 nucleus, m = 226 u = $226 \times 1.67.10^{-27}$ kg

Number of nucleus: N $= \frac{1\times10^{-3}}{226\times1,67\times 10^{-27}} = 2,7 \times 10^{21}$nucleus s

$\lambda = \frac{4,3\times10^{-4}}{365\times24\times3600} = 1,36 \times 10^{-11}$s $^{-1}$

$A = 1,36 \times 10^{-11} \times 2,7 \times 10^{21}$= 3.6×10^{10} Bq.

3) $A(t) = A_0 * e^{-\lambda t} \Rightarrow A(1000\,ans) = 3{,}6 \times 10^{10} \times e^{-1{,}36\times 10^{-11}\times 1000}$

$$A = 2{,}3 \times 10^{10}\,Bq$$

III.5.4. Independent disintegration (mixture of radionuclides)

If we find that the logarithmic plot of activity versus time is not a straight line, then this is an indication that the sample contains more than one radionuclide. In order to determine the individual decay constants of the mixture, it is necessary to measure the activity versus time, provided that the half-lives are moderately long and comparable to each other. The activity A of a mixture of radioisotopes is equal to the sum of the activities of the components:

$$A = \sum_j A_j = \sum_j A_{0j} e^{-\lambda_j t} = \sum_j A_j N_{0j}\, e^{-\lambda_j t}$$

If we consider a source containing two radioisotopes, we have:

$$A = \lambda_1 N_{01} e^{-\lambda_1 t} + \lambda_2 N_{02} e^{-\lambda_2 t}$$

If the half-lives (or λj) are sufficiently different while being neither too long nor too short and if the initial activities (or Noj) are comparable, plotting the variation of the activity as a function of time A = f(t) on a semi-logarithmic graph allows the two radioactive constants to be determined relatively precisely .

III.6. Applications of radioactivity

III.6.1. Carbon 14 dating

The period of a radionuclide is a constant independent of the number of nuclide or the temperature of the radioactive source, for this reason it is used to determine the age of rocks or archaeological pieces. Carbon-14 dating is thus based on the presence, in any living organism, of radiocarbon in tiny proportion (1.3.10 $^{-12}$ for the total C14/C ratio). From the moment an organism dies, exchanges with the outside ceasing, the quantity of radiocarbon it contains decreases over time according to a known exponential law. A sample of organic matter from this organism can therefore be dated by measuring the total C14/C ratio.

Example

An ancient bone fragment contains 80 g of carbon (mostly carbon 12) and has an activity of 0.75 Bq. How old is this bone fragment?

- carbon 12 is stable;
- The period of carbon 14: T = 5.7.10 ^{3} years;
- The mass of a carbon 12 nucleus: m = 12 u =12×1.67.10 $^{-27}$ Kg

Solution

We calculate the number of carbon 12 nuclei:

Number of nuclei: N (C12)$= \frac{80\times10^{-3}}{12\times1,67\times\,10^{-27}} = 4\times10^{24}$nucleus

We calculate the initial number of carbon 14 nuclei N $_{0}$ (C14):

We have

$\frac{^{14}C}{C_t} \Rightarrow N(C14) = \;\; 4\times10^{24}\times1,3\times10^{-12} = 5,2\times10^{12}$ nucleus s

We calculate the current number of carbon 14 nuclei N(C14):

The activity:$A = \lambda N \;\Rightarrow N = \frac{A}{\lambda}$

Gold $\lambda = \frac{ln2}{T} \Rightarrow N = \frac{A\times T}{ln2} \Rightarrow$

$$N(C14) = \frac{0,75\;\times5,7\times10^{3}\times365\times24\times3600}{ln2} = 1,9\times10^{11} noyaux$$

Finally, we calculate the age of the bone fragment.

We have

$$A = A_0 * e^{-\lambda t} \Longrightarrow\; N = N_0 * e^{-\lambda t}$$

$$\Longrightarrow\; \frac{N}{N_0} = e^{-\lambda t} \Longrightarrow\; ln\frac{N}{N_0} = -\lambda t = -\frac{ln2}{T} * t$$

$$t = \frac{ln\frac{N}{N_0}}{ln2} * T = \frac{ln\left[\frac{1,9\times10^{11}}{5,2\times10^{12}}\right]}{ln2} \times 5,7\times10^{3} \,=\, 2,7\times10^{4}\; ans$$

So the age of the bone fragment is 270,000 years.

III.6.2. Cancer treatment

Although high levels of X-rays and nuclear radiation cause cancer, such radiation can also be used to kill cancer cells, which are particularly sensitive to radiation because of their high growth rate. Using nuclear radiation in this way is called radiotherapy. The goal of radiotherapy is to deliver as high a dose as possible to the malignant tissue without causing serious injury to the surrounding healthy tissue.

III.6.3. Radioisotopes as tracers

Radioisotopes have the same chemical reactions as non-radioactive isotopes of the same element, but they have the advantage that their position can be located using appropriate detection equipment. Radiation can be used in different ways:

- as monitoring tools: markers (radioactive atoms) being introduced into an environment, it is then easy to detect the radiation they emit and to follow their fate (applications in medicine, science, food chain, environment, etc.),
- in imaging: the attenuation of a beam as it passes through matter depends on the materials passed through and their thicknesses (investigations in medicine, science, industry, etc.),

III.6.4. Energy profit (nuclear reactor)

A nuclear reactor is a set of devices comprising a vessel enclosing a "nucleus (fusion reaction)" in which a chain reaction can be initiated, moderated and controlled by human agents via protocols and devices for moderating nuclear fission and removing heat. The thermal energy is then transformed into electrical energy.

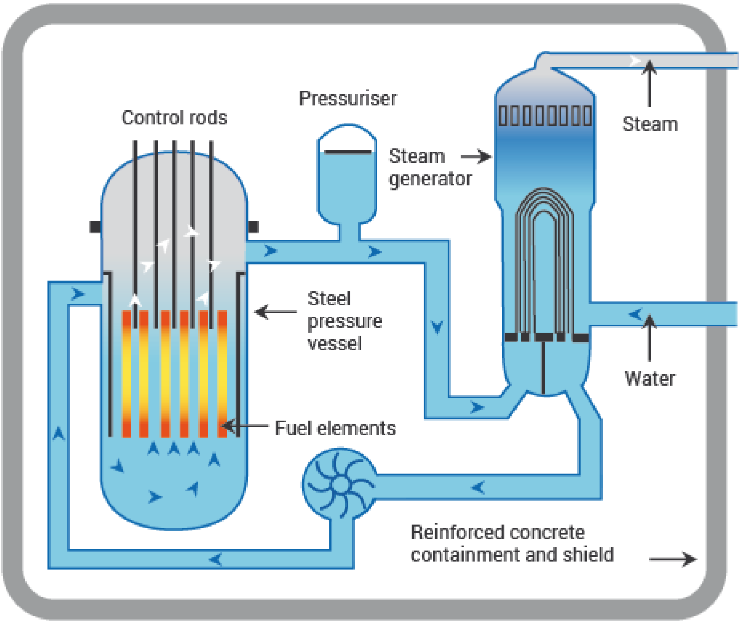


Figure III.3: Diagram of a nuclear reactor

III.6.5. Nuclear weapons

The energy of the atom is produced either by the fission of certain heavy atomic nuclei or by the fusion of certain light atomic nuclei depending on the type of bomb:

- **The "A-bomb** " is an atomic bomb known as a fission bomb since it results from the nuclear fission of nuclei such as uranium 235 or plutonium 239 when they encounter a neutron . It is necessary to trigger a chain reaction to obtain a nuclear explosion: for this, it is necessary to have a sufficient quantity of fissile material.
- **The "H-bomb"** is a so-called fusion hydrogen bomb. In fact, it results from the nuclear fusion between two nuclei such as deuterium and tritium (which are isotopes of hydrogen). Thermonuclear fusion is achieved by bringing the elements to very high temperatures.

III.7. Dangers

- Radiation can cause effects on human health:
    - The initial symptoms of irradiation are: nausea, vomiting, diarrhea, fever, headache, and erythema.

  - The risk of cancer
- Massive destruction (heat effect, blast, burns)
- Destruction or modification of animal and plant physiology (effect of radiation on cells).
- Environmental contamination due to nuclear waste and dust
- Risks of radiation leaks from nuclear reactors.

IV. Electronic structure of the atom

IV.1. Beginning of quantum theory

Classical physics (the set of physical theories validated until the end of the 19th century) has shown a weakness with regard to complicated scientific subjects.

- The Rutherford model accounts for the existence of different elements and isotopes, but it does not provide any basis for interpreting the diversity of properties of the elements (metals, non-metals, inert gases, etc.), nor for their valence. Furthermore, it does not allow the characteristics of the emission spectra of atoms to be justified.

  Other more efficient models have been imagined, including the quantum model or the Bohr model, in which the electron is considered as a moving particle. It is not the most modern of the atomic models, but its explanatory power is interesting.

- A black body is an idealized object that absorbs and emits all frequencies. We know, for example, that when the burner of an electric stove is heated, it first turns dull red and gradually becomes redder as the temperature increases. Classical physics has not been able to explain and predict the variation of radiation intensity as a function of temperature.

  The first person to offer a successful explanation of blackbody radiation was the German physicist Max Planck in 1900. He assumed that the radiation emitted by the blackbody was caused by the oscillations of electrons in the particles constituting matter. He made the revolutionary assumption that ***the energies of the oscillators are discrete and must be proportional to an integer multiple of the frequency*** or in equation form,

$$E = nh\upsilon ,$$

where E is the energy of an oscillator, n is an integer h is a constant of proportionality (Planck's constant, $h = 6.626.10^{-34}$ Js)), υ is the frequency.

The amount of energy that can be transferred is always an integer multiple of hu, 1h υ , 2h υ , 3h υ …etc. We then say that the energy is quantized,

- In 1905, Albert Einstein suggested that light energy is also quantized. It is formed by a stream of "particles", called photons, whose energy is:

$$E = h\upsilon = hc / \lambda ,$$

IV.1.1. Photoelectric effect

The photoelectric effect consists of the emission of electrons from a material subjected to light irradiation (Figure IV.1). The experiment was announced as follows: if a metal plate of an energy E_0 is illuminated with a monochromatic light of an energy E greater than the energy of the metal ($E > E_0$), the excess energy compared to the characteristic energy of the metal is dissipated in the form of kinetic energy taken by the electrons.

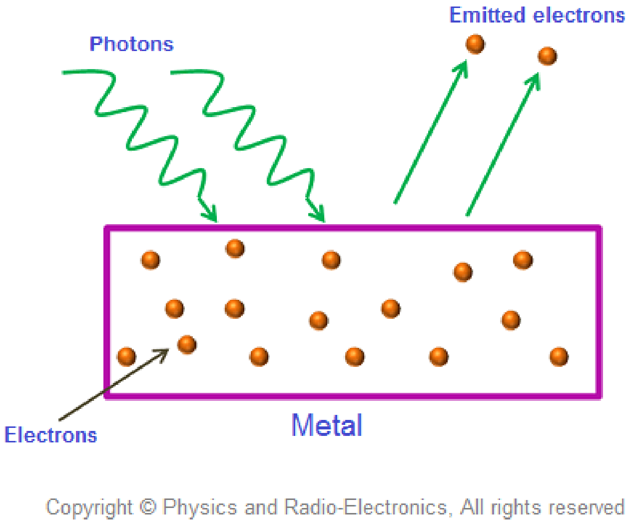


Figure IV.1: Photoelectric effect experiment

According to Einstein: light, in addition to having wave properties, can be considered as composed of corpuscles called photons, devoid of mass but possessing an energy $E = h\upsilon$. If a photon is absorbed by a material, the ejected electron has a kinetic energy (E_c) equal to the difference between the two characteristic energies.

$$E_c = E_{photon} - E_0 = \frac{1}{2} m v^2$$

IV.1.2. electromagnetic radiation

Electromagnetic radiation, of which visible light is an example, is a form of energy. Electromagnetic radiation is an electromagnetic wave due to a perpendicular electric field $\vec{E}$ and a magnetic field $\vec{B}$ oscillating in phase (Figure IV.2), can be diffracted and interfered with (James Clark Maxwell 1860)

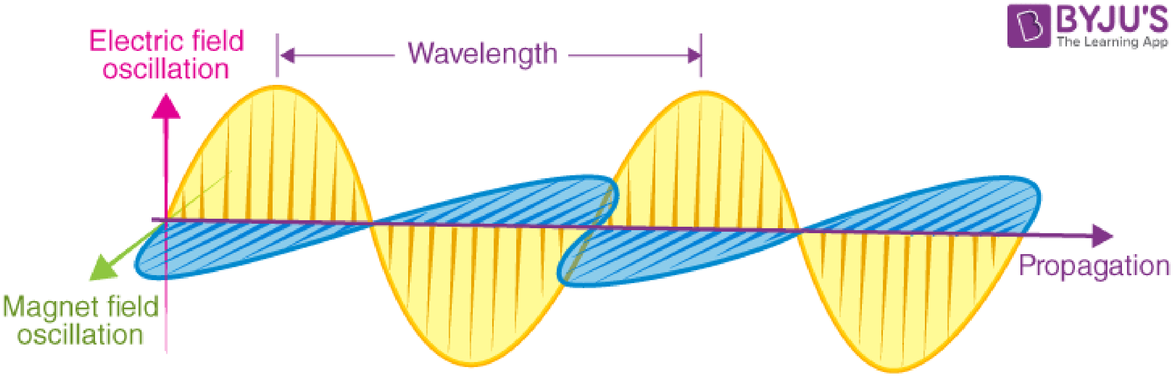


Figure IV.2: Electromagnetic wave

Electromagnetic radiation is also characterized by a propagation speed c which depends on the propagation medium, by a frequency υ (number of vibrations per second) and by a wavelength λ (distance traveled per vibration). As the frequency is the number of wavelengths traveled during one second, these three quantities are linked by the following relation:

$$c = \lambda \times \nu = \frac{\nu}{\bar{\nu}}$$

c: speed of light in vacuum is 2.997925. 10^8 m/s

λ: wavelength (nm).

ν: frequency (Hz).

$\bar{\nu}$: wave number (cm^{-1}) knowing that $\bar{\nu} = \frac{1}{\lambda}$

Frequency and wavelength can have various values, from which particular areas of electromagnetic radiation are distinguished, as shown in Figure IV.3.

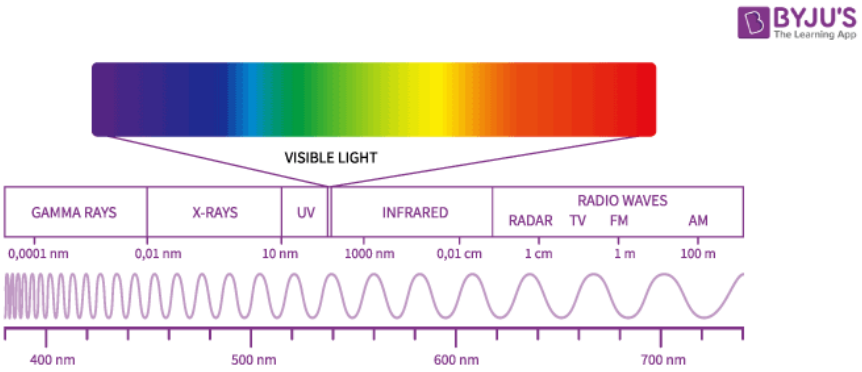


Figure IV.3: Electromagnetic spectrum. Visible light (bottom magnification) is only a small portion of the spectrum.

IV.2. Wave–matter interaction

IV.2.1. Emission and absorption of radiation by matter

Energy exchanges can occur between matter and radiation, in two directions (Figure IV.4):

- Emission: Are phenomena of radiation emission due to a return to the stable state of one or more atoms.

  Example: The light emitted by the sun and the flame.

- Absorption: This is an absorption phenomenon due to the passage to the excited state of one or more atoms.

  Example: Performing an X-ray on a part of the human body is done by absorbing X-rays,

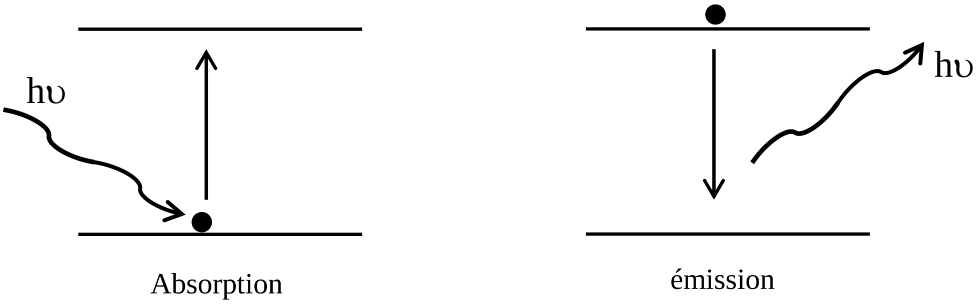


Figure IV.4: Diagram of radiation absorption and emission phenomena

IV.2.2. Continuous and discontinuous spectrum

A **continuous spectrum** has continuity between spectral lines, for example, the rainbow contains all colors with a continuous transition from ultraviolet to infrared it is a continuous spectrum, because the wavelengths form an uninterrupted whole of colors (Figure IV.5.a).

A **discontinuous spectrum** does not exhibit continuity between spectral lines (Figure IV.5.b), for example, light emitted by an electric arc.

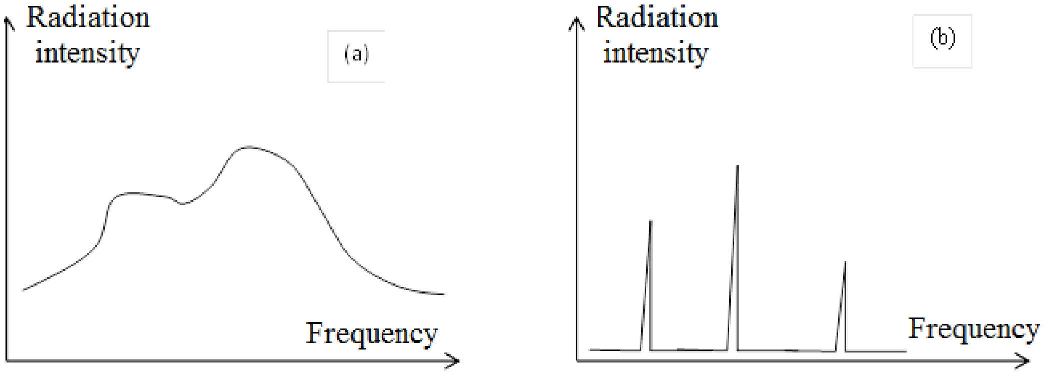


Figure IV.5: Variation of the intensity of radiation as a function of frequency. a) continuous spectrum, b) discontinuous spectrum

IV.2.3. Hydrogen spectrum

When a high voltage is applied to hydrogen atoms in the gaseous state under very low pressure, it leads to the emission of light. The resulting beam is decomposed by a prism to give lines corresponding to characteristic wavelengths in the IR , UV and Vis can be detected using a photographic plate (Figure.IV.6)

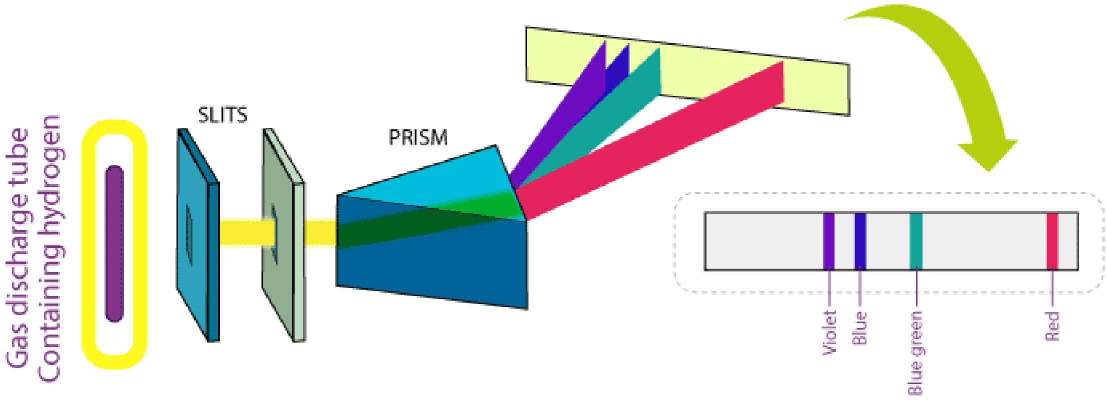


Figure.IV.6: Hydrogen line spectrum

Atomic hydrogen acquires energy; the atoms enter an unstable excited state. Then they return to the ground state (lower energy) by emitting photons. Each line of the spectrum corresponds to a transition between 2 energy levels (Figure IV.7).

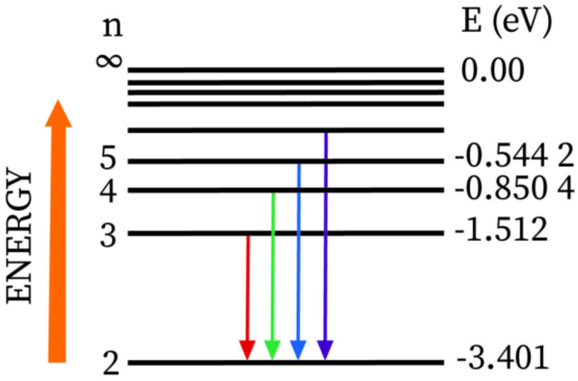


Figure IV.7: Transitions to level n=2 (Balmer series)

In 1885, Johann Jacob Balmer published an empirical formula for calculating the wavelengths of the hydrogen atom spectrum. He found that the wavelengths of the red, green, and blue lines emitted by hydrogen satisfied this equation.

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

R_h : Rydberg constant=1.097373 10^{7} m^{-1} .

n: positive integer greater than 2

Example

Calculate the emission wavelength of hydrogen for a transition between level 2 and level 5.

Solution

$$\frac{1}{\lambda} = 1{,}097373\ 10^{7}\ \times \left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 4{,}34\ 10^{-7} = 434\ 10^{-9} m = 434\ nm$$

The spectrum of hydrogen is a discontinuous spectrum, since it presents only a few lines in the visible and without continuity, called the Balmer series lines. This series takes into account several values of n (n=3, 4, 5, 6 and 7) corresponding to the wavelengths **656.5** , **486.1** , **434** , **410.1** and **397** nm respectively.

As we have shown in this short, the electromagnetic spectrum does not only contain the visible domain but other spectral regions such as ultraviolet and infrared. Of which hydrogen has emission lines that did not satisfy the previous equation.

For this reason and in 1888 the physicist Johannes Rydberg generalized the Balmer formula to satisfy all the emission lines of the hydrogen atom. The new formula called **Rydberg equation.**

$$\frac{1}{\lambda} = \mathrm{R_h}\ \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

n_f and n_i are integers such that $n_f < n_i$

The other transitions were discovered and each series was named after its owner. Table IV.1 shows the names of the series and the spectral domains they occupy according to the quantum number.

Table IV.1: Spectral series of the hydrogen atom

Series	transition	Spectral domain
Lyman	$n_f =$ and $n_i > 1$	RX and UV
Balmer	$n_f = 2$ and $n_i > 2$	Visible
Paschen	$n_f = 3$ and $n_i > 3$	IR
Brackett	$n_f = 4$ and $n_i > 4$	IR
Pfund	$n_f = 5$ and $n_i > 5$	IR

IV.3. Bohr Model

IV.3.1. Quantum theory

According to the classical model the electron rotates around the nucleus emitting light, this means that the energy of this electron will gradually decrease and it should gradually approach the nucleus and finally fall on it. As a result the atoms become unstable, which is in contradiction with reality.

In 1913, Niels Bohr proposed a model of the atom that could resolve these contradictions based on Planck's theory.

IV.3.2. Bohr's postulates

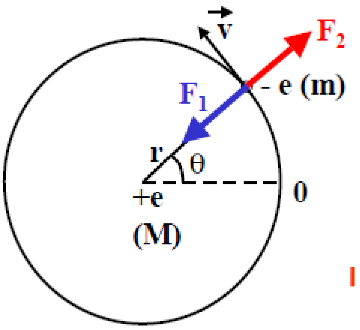
Niels Bohr was the first to make the connection between spectra and the quantum ideas of Planck and Einstein. He constructed a new model of the atom, whose essential characteristics are as follows:

- In the atom, the nucleus is stationary while the electron of mass m moves around the nucleus in a circular orbit of radius r.

- The electron can only be in privileged orbits without emitting energy; these are called "stationary orbits".
- When an electron passes from one level to another it emits or absorbs energy.

  $\Delta E = h\nu = |E_f - E_i|$

- The electron is subject to two forces:



The Coulomb force of attraction

$$\boxed{F_1 = \frac{1}{4\pi\varepsilon_o}\frac{e^2}{r^2}}$$

$\varepsilon_0 = 8.85\ 10^{-12}$ C2 N^{-1} m^{-2} (vacuum permittivity); r = orbit radius

The electron is also subjected to the centrifugal force F2 $\boxed{F_2 = m\,\mathbf{a} = mv^2 / r}$

- At equilibrium F1 = F2 $\boxed{\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r^2} = \frac{mv^2}{r}} \Rightarrow \boxed{r = \frac{1}{4\pi\varepsilon_o}\frac{e^2}{mv^2}}$ **(1)**

Total energy = Potential energy + Kinetic energy

Potential energy $E_p = -\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}$

Kinetic energy $E_c = \frac{1}{2}mv^2 = \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}\right)$

Total energy $E = -\frac{1}{2}\left(\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}\right)$

- Assuming that the electron is described by a wave and that an integer number of wavelengths must fit the circumference of the electron orbit, we have the following equation:

$$\boxed{2\pi r = n\lambda} \quad (n = 1, 2, 3...)$$

- Louis de Broglie: Every particle in motion is associated with a wavelength.

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

- angular momentum of the electron can only take integer values (quantization of angular momentum):

$$\vec{L} = \mathrm{mvr} = \frac{nh}{2\pi}$$

We know that the vector product of two vectors gives a vector perpendicular to them.

$$\vec{L} = \vec{p} \wedge \vec{r}$$

p is the momentum equal to mass times velocity (p=m*v)

$$\vec{L} = m * \vec{v} \wedge \vec{r} \implies \vec{L} = m\vec{v} * \vec{r} sin90 = mvr$$

Bohr suggested a relationship between the angular momentum of the electron and the quantum number n: the variation of implies a variation in L. He translated this result into the following relationship

$$\vec{L} = \mathrm{mvr} = \frac{nh}{2\pi}$$

h: Planck's constant and n: natural number.

Example

The energy levels of the hydrogen atom have the value in eV: En = – 13.6 / n2.

What is the wavelength of the radiation λ emitted during de-excitation from level E4 to level E2? To which domain does this radiation belong?

Data: $h = 6.626 . 10^{-34}$ Js ;

$c = 3.00 . 10^{8}$ ms^{-1} ; 1.00 eV = $1.60. 10^{-19}$ J.

Solution

When de-energizing from level E4 to level E2,

a photon of energy $h\upsilon = |E_2 - E_4|$is emitted. Now $h\,\upsilon = hc / \lambda$

The wavelength of the radiation λ associated with this photon is deduced from this:

$$\lambda = \frac{hc}{|E_2 - E_4|}$$

Or numerically:

$$\lambda = \frac{6{,}626\,.\,10^{-34} 3.\,10^{8}}{1{,}6.\,10^{-19}\left|\frac{-13{,}6}{4} + \frac{13{,}6}{16}\right|}$$

$\lambda = 4.87.10^{-7}$ m = 487 nm

The corresponding radiation belongs to visible light (400 to 800 nm). It is blue in color.

IV.4. The hydrogen atom according to the Bohr model

The simplest atom to study according to this model is the hydrogen atom, because it has only one electron circulating around a nucleus that contains a proton. According to Bohr's model the electron is at a distance from the nucleus, rotating around it in a circular fashion as shown in Figure IV.9.

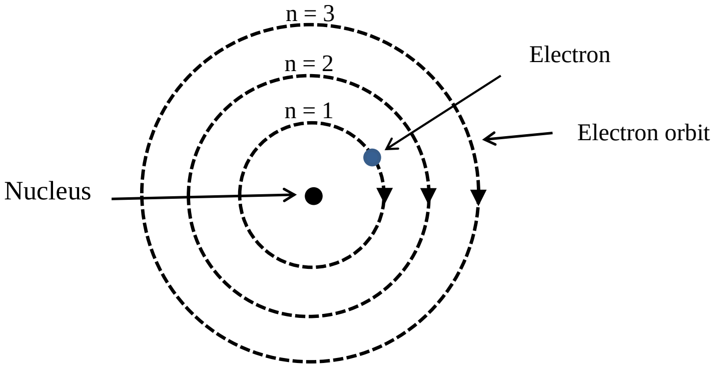


Figure IV.9: Diagram of the hydrogen atom according to the Bohr model

The electron can be on an infinite number of possible orbitals around the nucleus, each orbital is at a specific distance or radius from the nucleus.

IV.4.1. Radius of the hydrogen atom

For the hydrogen atom we consider a single electron of mass m rotating around a central nucleus of positive charge +e and mass M such that M >> m (so the nucleus is assumed to be fixed). The electron and the nucleus are separated by a distance r which is the radius of the orbital (Figure IV. 10).

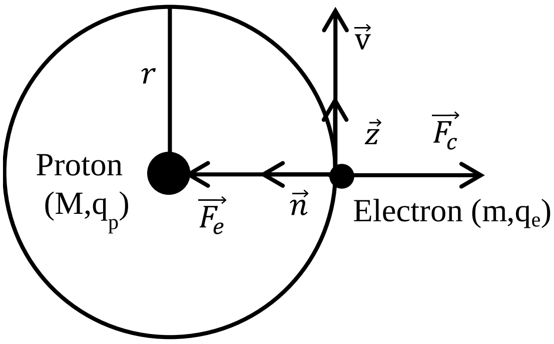


Figure IV.10. Diagram shows the trajectory of the electron and the forces applied to it **.**

The forces that can intervene are

The gravitational interaction force F_g :

$$F_g = G * \frac{m_e * M_p}{r^2}$$

This force is negligible due to the mass of the electron which is of the order of 10^{-31} kg

Centrifugal force.

$$\overrightarrow{\|F_c\|} = m\gamma = m\frac{v^2}{r}$$

For a circular trajectory $\gamma = \frac{v^2}{r}$

The Coulomb force of attraction (electrostatic force F_e)

$$\overrightarrow{\|F_e\|} = \frac{1}{4\pi\varepsilon_0}\frac{|q_p q_e|}{r^2}$$

$\varepsilon_0 = 8.85\ 10^{-12}\ C^2\ N^{-1}\ m^{-2}$ (vacuum permittivity)

In balance

$$|F_e| = |F_c| \Rightarrow \frac{1}{4\pi\varepsilon_0}\frac{|q_p q_e|}{r^2} = m\frac{v^2}{r} \Rightarrow$$

$$\frac{1}{4\pi\varepsilon_0}\frac{|q_p q_e|}{r} = mv^2 \Rightarrow r = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{mv^2} = k\frac{e^2}{mv^2}$$

According to the Bohr equation, the quantization of the orbital angular momentum ($\vec{L}$) is written:

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

We replace v in the relation of r we obtain

$$r = k\frac{e^2}{m}\frac{4m^2r^2\pi^2}{n^2h^2} \Rightarrow$$

$$r = \frac{h^2}{4k\pi^2me^2}n^2$$

and since h , π , k, m and e are constants then r only depends on the value of the positive number n called the principal quantum number, i.e.:

$$r_n = \frac{h^2}{4k\pi^2me^2}n^2$$

n: principal quantum number

r: the distance between the nucleus and the electron

h: Planck's constant

ζ_0 : the permittivity of vacuum

m: mass of the electron

e: the load

The orbit closest to the proton is that corresponding to the n = 1 shell.

The radius of this orbit is.

$$r_1 = \frac{h^2}{4k\pi^2 me^2} = 0{,}52910^{-10}m$$

It is called the "Bohr ray"

The expression for r is written as:

$$r_n = r_1 \times n^2$$

IV.4.2. Energy of the hydrogen atom

The atom has been defined as a set, formed by a nucleus surrounded by electrons. The latter are linked to the nucleus by the influence of potential energy and kinetic energy.

We have the total energy (E_T) equal to the sum of the potential energy (E_P) and the kinetic energy (E_C) as follows:

$$E_T = E_P + E_C$$

The potential energy between a charge +e and a charge −e is given by the expression

$$E_P = -\,k\frac{e^2}{r}$$

$$E_C = \frac{1}{2}mv^2 = \frac{1}{2}\left(k\ \frac{e^2}{r}\ \right)$$

$$E_T = -\,k\frac{e^2}{r} + \frac{1}{2}k\ \frac{e^2}{r}$$

$$\Rightarrow\ E_T = -\ \frac{1}{2}k\ \frac{e^2}{r}$$

The total energy equation now depends on the orbital radius, by replacing r with its value in the equation for E_t, the total energy becomes dependent on the quantum number n:

$$E_n = -\frac{2\pi^2 k^2 me^4}{h^2} \times \frac{1}{n^2}$$

Knowing that $\frac{2\pi^2 k^2 me^4}{h^2} = -13{,}6$

$$E_n = -13{,}6\ \times \frac{1}{n^2}$$

For n=1 E_n = -13.6 eV ground state energy of the electron

For $n=\infty$ $E_n = 0$ eV ionized state (the electron has left the atom)

Transitions between electronic levels

Electronic transitions between energy levels are at the origin of the spectral lines emitted by atoms. In other words, the electronic transition is the passage of an electron between energy levels. A passage from a lower energy level to a higher level is called absorption, on the other hand the opposite is called emission (spectrum of hydrogen. Figure IV.11).

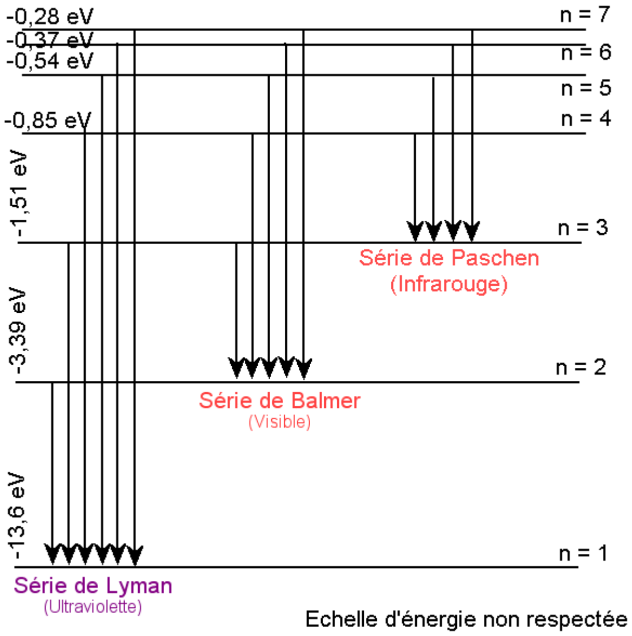


Figure IV.11: Electronic transitions of the hydrogen atom.

In the hydrogen spectrum we have an electronic transition from a higher energy level to a lower level, which caused a release of energy (ΔE) in the form of light (spectral line). This energy can be calculated by the following equation:

$$\Delta E = E_f - E_i = h \times R_h \times c \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

IV.4.3. Applications to hydrogenoids

A hydrogenoid is a monoatomic entity having only one electron ($_1H$, $_2He^+$, $_3Li^{2+}$ …). A hydrogenoid can be written as follows $_ZX^{(Z-1)+}$ let us know that X is the chemical element and Z the atomic number. A hydrogenoid leads to results similar to those of hydrogen. Indeed, for the level n considered, we have:

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

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

$$\nu = \mathrm{R_h} \times \mathrm{c} \times Z^2 \left(\frac{1}{\mathrm{n_f^2}} - \frac{1}{\mathrm{n_i^2}}\right)$$

Bohr developed a model that allowed him to theoretically calculate the wavelengths of radiation emitted by hydrogen.

Application exercises

Exercise 1

1. Establish for a hydrogen atom (nucleus of charge + Ze around which an electron gravitates), the formulas giving:

a- The radius of the orbit of rank n.

b- The energy of the nucleus-electron system corresponding to this orbit.

c- Express the radius and the total energy of rank n for the hydrogenoid as a function of the same quantities relative to the hydrogen atom.

2. Calculate in eV and joules the energy of the first four levels of the hydrogenoid ion Li2+, knowing that in the ground state, the energy of the nucleus-electron system of the hydrogen atom is equal to -13.6 eV.

3. What energy must a Li2+ ion absorb for the electron to pass from the ground level to the first excited level?

4. If this energy is supplied in the form of light, what is the wavelength l1-2 of the radiation capable of causing this transition?

We give: Li (Z=3) 1eV= 1.6.10-19 Joules

h= 6.62.10-34 Js c = 3.108 ms-1

Solution

1. Balance of forces: Two collinear forces in opposite directions are exerted on the electron, Fe (electrostatic) and Fc (centrifugal due to motion).

$$\overrightarrow{\|F_e\|} = \frac{Z}{4\pi\varepsilon_0}\frac{|q_p q_e|}{r^2} \qquad \overrightarrow{\|F_c\|} = m\frac{v^2}{r}$$

For the electron to remain in an orbit of radius r, it is necessary that: | F_e |=| F_c | then see the course.

2. For a hydrogenoid $E_n = -\frac{13{,}6}{n^2}Z^2$This implies that the energy corresponding to the four levels of Li $^{2+}$: Z=3 equals

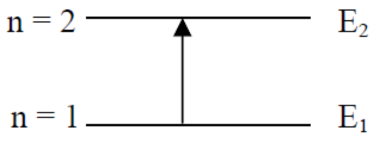
n= 1 E1 = -122.6 eV = - 19.6.10 $^{-18}$ J

n= 2 E2 = -30.6 eV = -4.9.10 $^{-18}$ J

n= 3 E3 = -13.6 eV = -2.18.10 $^{-18}$ J

n=4 E4= -7.65 eV = -1.22.10 $^{-18}$ J

3. Let us imagine the transition between two energy levels n=1 and n=2 (absorption)



Absorbed energy: ΔE = E2 – E1 = -30.6-(-122.4) = 91.8eV

4. Conservation of energy

$$\Delta\mathrm{E} = \left(\frac{\mathrm{hc}}{\lambda}\right) \Rightarrow \lambda = \left(\frac{\mathrm{hc}}{\Delta\mathrm{E}}\right)$$

$\lambda = (6.62.10^{-34} \times 3.10^{8})/(91.8 \times 1.6.10^{-19}) = 1.35.10^{-8}$ m = 135 Å.

(Radiation in the ultraviolet range)

Exercise 2

The energy levels of the hydrogen atom have the value in eV: En = – 13.6 / n2.

What is the wavelength of the radiation λ emitted during de-excitation from level E4 to level E2?

What area does this radiation belong to ?

Data: $h = 6.626 . 10^{-34}$ Js ;

$c = 3.00 . 10^{8}$ ms^{-1} ; 1.00 eV = $1.60. 10^{-19}$ J.

Solution

When de-energizing from level E4 to level E2, an energy photon $h\upsilon = |E_2 - E_4|$is emitted.

Or $\quad h\upsilon = hc / \lambda$

The wavelength of the radiation λ associated with this photon is deduced from this:

$$\lambda = \frac{hc}{|E_2 - E_4|}$$

Or numerically:

$$\lambda = \frac{6{,}626 . 10^{-34} 3. 10^{8}}{1{,}6. 10^{-19} \left|\frac{-13{,}6}{4} + \frac{13{,}6}{16}\right|}$$

$\lambda = 4.87.10^{-7}$ m = 487 nm

The corresponding radiation belongs to visible light (400 to 800 nm). It is blue in color.

IV.5. Inadequacy of the Bohr model

- The relationship used to calculate the frequency of the transition between two energy levels is not valid for a polyelectronic atom .

- This theory proves insufficient to explain the splitting of spectral lines observed when applying an intense magnetic field (Zeeman effect) or an intense electric field (Starck effect).
- the energy of electrons is quantized it can only take certain values this idea is preserved
- the movement of electrons takes place on circular or elliptical trajectories this idea is abandoned and replaced by the probability of presence.

Sommerfeld model

This theory made it possible to introduce a certain number of fundamental notions:

- Separation of the quantization of energy from that of kinetic momentum

- Degeneracy of spectroscopic terms

IV.6 . Quantum numbers

IV.6.1. The principal quantum number n

The principal quantum number n describes the principal energy level of an occupying electron. This number defines the size of the orbital and as we have already seen, the energy of the system is written as a function of the principal quantum number n, so this energy is quantized using this number:

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

n is an integer:

n = 1: K layer

n = 2: L layer

n = 3: M layer

n = 4 : layer N

n = 5: layer O

n = 6: P layer

n = 7: Q layer

IV.6.2. The secondary (or azimuthal) quantum number l

The secondary quantum number refers to the shape of the region in space that an electron occupies. This number (l) can take integer values from 0 up to and including (n - 1).

This number defines the electronic subshells

l = 0: s orbitals,

l = 1: p orbitals,

l = 2: d orbitals,

l = 3: f orbitals.

The azimuthal quantum number "l" quantifies the norm of the angular momentum $\| \vec{L} \|$,

$$\| \vec{L} \| = \sqrt{l.(l+1)}\,.\,\hbar$$

IV.6.3. The tertiary (or magnetic) quantum number m_l

number is an integer, it can take negative values between –l and +l. Thus, when the secondary number l equals 3, the magnetic number m_l can take the following seven values: -3, -2, -1, 0, +1, +2, +3. This number defines the orientation of the atomic orbital and it quantized $\overrightarrow{L_Z}$, component of $\vec{L}$on the z axis.

$$\overrightarrow{L_Z} = m_l * \hbar$$

IV.6 .4. The spin quantum number s (or m_s)

The spin quantum number is linked to the electron's own magnetism. It can only take two equal and opposite values: -1/2 +1/2. This number defines the rotation of the electron on itself (intrinsic kinetic momentum).

Table IV.2: Admissible values of quantum numbers at n = 3

n	L 0 up to and including (n - 1).	m_l between –l and +l.	S(m_s)	Number of electrons main layer $2n^2$	Number of electrons Undercoat (4l+2)
1	0	0	-1/2, +1/2	2	2
2	0 1	0 -1, 0, +1	-1/2, +1/2 ±1/2 for each value of m_l	8 8	2 6
3	0 1 2	0 -1, 0, +1 -2, -1, 0, +1, +2	-1/2, +1/2 ±1/2 for each value of m_l	18 18 18	2 6 10
4	0	0	-1/2, +1/2	32	2

	1	-1, 0, +1	±1/2 for each value of m_l	32	6
	2	-2, -1, 0, +1, +2		32	10
	3	-3, -2, -1, 0, +1, +2, +3		32	14

IV.7 . Wave model of the atom

Bohr's quantum model has two main ideas: the electron's energy is quantized and its motion occurs on stable, circular trajectories. The latter was replaced by the probability of presence in a new model of the atom called the wave model. This model was developed by the Austrian Erwin Schrödinger who studied the structure of the atom by considering the electron as a wave.

IV.7.1. Louise De Broglie's Hypothesis

To explain the photoelectric effect, Einstein hypothesized that light, generally perceived as a wave, can be considered as a massless corpuscle. In 1924, Louise de Broglie proposed to associate a free electron of mass (m) moving at a speed (v) with a wave of wavelength (λ) defined by the relation:

$$\lambda = \frac{h}{m * v} = \frac{h}{p}$$

Knowing that (p) expresses the quantity of movement.

IV.7.2. Heisenberg's uncertainty principle

In our daily life we can determine the position and speed of a car simultaneously, but this is not the case for microscopic particles. Heisenberg's inequality is as follows: **Not all physical quantities of the macroscopic world are simultaneously observable in the submicroscopic world.**

Example: If a mass m is moving on a trajectory with a speed v, at time t; we cannot know exactly both its position and its momentum p. If we call Δ x the uncertainty on its position and Δp the uncertainty on its momentum p.

$$\Delta x * \Delta p \geq \frac{h}{2\pi}$$

$$\Delta p = m * \Delta v$$

$$\Delta x * \Delta v \geq \frac{h}{2\pi * m}$$

For one thing, we can no longer ignore the two terms. Δx and Δp

IV.7.3. The wave function and Schrödinger equation

The wave model takes the point of view of considering the electron as a wave and not as a particle (Figure IV.12). A moving particle is associated with a wave whose amplitude depends on the space and time coordinates of the particle, i.e. $\Psi(x, y, z, t)$. Ψ(psi) is the wave function of the particle (electron).

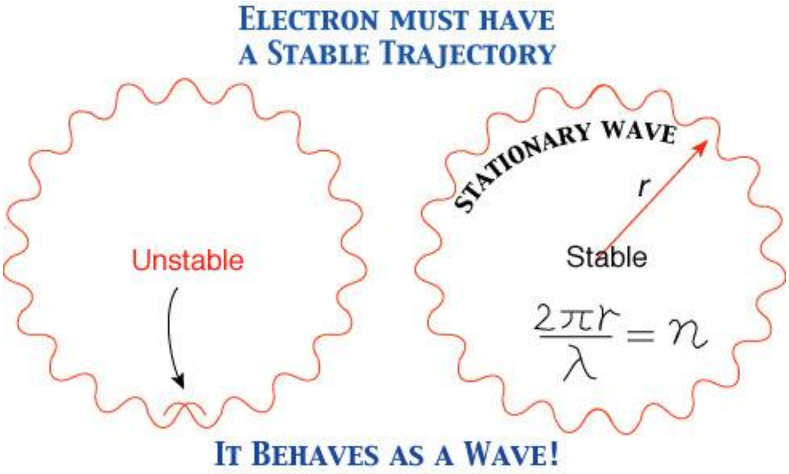


Figure IV.12: Representation of the trajectory of an electron around the nucleus and its associated wave

IV.7.3.1. Schrödinger model

Generally, the Schrödinger model can be summarized in the following points:

- The behavior of the electron in the atom is described using a standing wave (a wave that has at least two nodes separated by a distance $\frac{\lambda}{2}$(Figure IV.13))

Figure IV.13: Diagram of a standing wave

- Each wave function (Ψ) corresponds to an energy E_n
- As a consequence of the first two points, the energy of an electron is quantized , that is to say that the electron only has certain values.
- The square of the wave function (Ψ^2) is related to the probability of finding the electron dP in a given region of space. The probability of finding the electron in a volume dV at the point M(x, y, z) is written :

  $$dP = \Psi^2 \times dV$$

  The ratio dP / dV = $\Psi^2$is called the probability density of the presence of the electron at the point considered, also called "the electronic density".

  For an infinite volume we are certain to find it there and therefore the probability equal to 1 is **the normalization condition:**

  $$\int_{espace} \Psi^2 \times dV = 1$$

- Other boundary conditions:
  - Ψ(x ,y,z,t) must be continuous at all points,
  - Ψ(x ,y,z,t) must be finite at all points,
  - Ψ(x ,y,z,t) →0 when x or y or z → ∞
- Schrödinger's theory precisely defines the energy of the electron. According to the principle Heisenberg's model, it is impossible to locate the electron precisely. The model gives a probability of finding it at a given point in space in a given energy state. The region in which it is most likely to be found is called **an orbital** . Depending on the variation of Ψ^2we can have different orbitals.
- Solving the Schrödinger equation for an electron in three-dimensional space necessarily involves three integers, the quantum numbers n , l and m_l : $\Psi_{n,l,m}$. These numbers obey special rules.

IV.7.3.2. Wave function

The Schrödinger equation can be written from the equation of motion of a particle. We consider the vibrational motion of the electron which is on a stationary orbital (same amplitude "A" and same λ) (Figure IV.14)

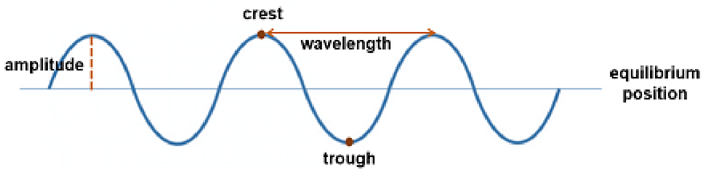


Figure IV.14: Diagram of wave propagation

The standing wave is expressed as:

$$\psi(x) = A * sin\frac{2\pi}{\lambda}x$$

The first and second derivatives of this equation give:

$$\frac{d\psi(x)}{dx} = A.\frac{2\pi}{\lambda}.cos\frac{2\pi}{\lambda}x$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}A.sin\frac{2\pi}{\lambda}x = -\frac{4\pi^2}{\lambda^2}.\psi(x)$$

We obtain a second order differential equation:

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}.\psi(x) = 0$$

We have $\lambda = \frac{h}{p} = \frac{h}{mv} \rightarrow \lambda^2 = \frac{h^2}{m^2v^2} \rightarrow \frac{1}{\lambda^2} = \frac{m^2v^2}{h^2}$

Multiplying both sides of the equation by 4π, gives:

$$\frac{4\pi^2}{\lambda^2} = 4\pi^2\left(\frac{m^2v^2}{h^2}\right)$$

Let E be the total energy of the particle, Ec its kinetic energy and Ep its potential energy:

$$E = E_c + E_p \Rightarrow E - E_p = \frac{1}{2}mv^2 \Rightarrow 2m(E - E_p) = m^2v^2$$

from where

$$\frac{4\pi^2}{\lambda^2} = 8\pi^2 m\left(\frac{E - E_p}{h^2}\right)$$

$$\text{Hence } \frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}(E - E_p)\psi(x) = 0$$

The one-dimensional Schrödinger equation.

Generalizing to three dimensions of space and introducing the Laplacian operator:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ with } E_p = E_x + E_y + E_z$$

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\Delta + E_p$$

$$\Delta\psi + \frac{8\pi^2 m}{h^2}(E - E_p)\psi = 0$$

Three-dimensional Schrödinger equation, it is written in symbolic form:$\hat{H}\psi = E\psi$

$\hat{H}$: represents an operator, called Hamiltonian, by applying it to the function ψ transforms it into another function, its expression depends on the system considered

$E\psi$: it is a product of the function $\psi$and its associated energy E.

The solutions of the Schrödinger equation must satisfy a number of conditions: the psi function must be unique, finite and continuous with respect to x , y and z, it must satisfy the normalization condition, which is achievable only for certain values of the energy called eigenvalues. We then speak of a **quantization of the energy of the system** .

IV.8. Resolution of the Schrödinger equation in the case of the hydrogen atom

The hydrogen atom consists of a proton and an electron in interaction. The mass of the proton being nearly 2000 times that of the electron, the proton is considered fixed (Born-

Oppenheimer approximation); the frame of reference originating from the nucleus is therefore considered Galilean (Figure IV.15) .

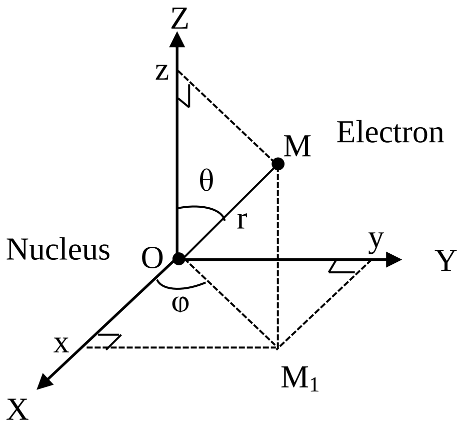


Figure IV.15: Presentation of the electron by spherical coordinates

The forces applied to the electron are the electrostatic force $\overrightarrow{f_{el}}$exerted by the nucleus on it and the gravitational force which is negligible compared to the electrostatic force.

$$\overrightarrow{f_{el}} = +\frac{(-e).(+e)}{4\pi\varepsilon_0}.\frac{\overrightarrow{u_r}}{r^2}$$

Space is related to a trihedron (O ,x,y,z) whose origin coincides with the position of the nucleus. For an isolated hydrogen atom, space is isotropic (does not depend on the direction) and the position of the axes is arbitrary. Since, on the other hand, the potential energy of the system is of electrostatic origin and only involves the nucleus/electron distance, it is convenient to use the spherical coordinates of origin O.

Solving the Schrödinger equation for this system leads to wave functions ψdepending on the variables r, θ and φ. The position of the point M is identified in Cartesian coordinates by the triplet (x ,y,z). We can also use the triplet (r, θ, φ) in which θ and φ are angle measures while r is a distance: θ = (Oz,OM) ; φ = (Ox,OM $_1$). To cover the entire space, it is sufficient that r varies from 0 to +∞, θ varies from 0 to π and φ varies from 0 to 2π.

The relationship between the Cartesian coordinates M and its spherical coordinates is written as:

$z= r . \cos \theta$

$x= r . \sin \theta . \cos \varphi$

$y= r . \sin \theta . \sin \varphi$

IV.8.1. Wave functions of the hydrogen atom

The function $\psi(r,\theta,\varphi)$is the product of three functions:

$$\psi(r,\theta,\varphi)= R(r) . \Theta(\theta) . \Phi(\varphi)$$

A: The radial part of psi, because it only depends on the variable r.

$\Theta(\theta) . \Phi(\varphi)$: The angular part of the wave function, since it depends only on the angular coordinates θ and φ, often called $Y(\theta, \varphi)$.

Solutions to the Schrödinger equation for the hydrogen atom give wave functions, which describe the different states available to a single electron of hydrogen. Each of these possible states is described by four quantum numbers. These quantum numbers play an important role in describing the energy levels of electrons and the shapes of orbitals that describe the distributions of electrons in space.

The wave functions of the hydrogen atom, or atomic orbitals, are characterized by the quantum numbers n, l and m_l:

$$\psi_{n,l,m_l}(r,\theta,\varphi)= R_{n,l}(r). \Theta_{l,|ml|}(\theta) . \Phi_{ml}(\varphi)$$

As we can see R(r) depends on the numbers n and l, $\Theta(\theta)$ depends on the numbers l ,$|m_l|$ and $\Phi_{ml}(\varphi)$ depends on the quantum numbers m_l.

IV.8.2. Expressions of the orbitals of the hydrogen atom

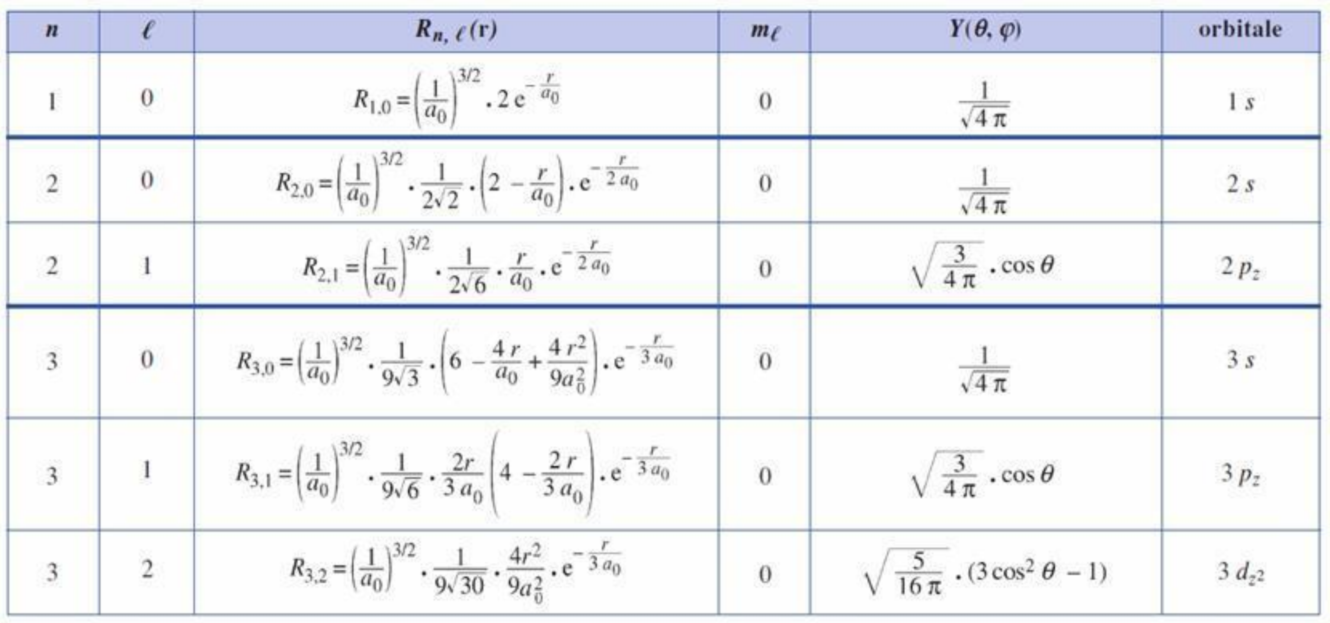
The mathematical expression of the radial and angular parts of the wave function is written as follows:

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\,(n+l)!}}\, e^{-\left(\frac{r}{na_0}\right)} r^l L_{n-l-1}^{2l+1}(r)$$

$$Y_{l,m_l}(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m_l)!}{(l+m_l)!}}\, P_l^{m_l}(\cos\theta) e^{i m_l \phi}$$

Table IV.3 gives the expressions for the radial part and the angular part of some orbitals of the hydrogen atom.

Table IV. 3: Radial and angular parts of some wave functions of the hydrogen atom. These expressions involve the Bohr radius a $_0$ = 52.9 pm.



n	ℓ	$R_{n,\ell}(\mathrm{r})$	m_ℓ	$Y(\theta, \varphi)$	orbitale
1	0	$R_{1,0}=\left(\frac{1}{a_0}\right)^{3/2}.2\,\mathrm{e}^{-\frac{r}{a_0}}$	0	$\frac{1}{\sqrt{4\pi}}$	$1\,s$
2	0	$R_{2,0}=\left(\frac{1}{a_0}\right)^{3/2}\cdot\frac{1}{2\sqrt{2}}\cdot\left(2-\frac{r}{a_0}\right).\mathrm{e}^{-\frac{r}{2a_0}}$	0	$\frac{1}{\sqrt{4\pi}}$	$2\,s$
2	1	$R_{2,1}=\left(\frac{1}{a_0}\right)^{3/2}\cdot\frac{1}{2\sqrt{6}}\cdot\frac{r}{a_0}.\mathrm{e}^{-\frac{r}{2a_0}}$	0	$\sqrt{\frac{3}{4\pi}}.\cos\theta$	$2\,p_z$
3	0	$R_{3,0}=\left(\frac{1}{a_0}\right)^{3/2}\cdot\frac{1}{9\sqrt{3}}\cdot\left(6-\frac{4r}{a_0}+\frac{4r^2}{9a_0^2}\right).\mathrm{e}^{-\frac{r}{3a_0}}$	0	$\frac{1}{\sqrt{4\pi}}$	$3\,s$
3	1	$R_{3,1}=\left(\frac{1}{a_0}\right)^{3/2}\cdot\frac{1}{9\sqrt{6}}\cdot\frac{2r}{3a_0}\left(4-\frac{2r}{3a_0}\right).\mathrm{e}^{-\frac{r}{3a_0}}$	0	$\sqrt{\frac{3}{4\pi}}.\cos\theta$	$3\,p_z$
3	2	$R_{3,2}=\left(\frac{1}{a_0}\right)^{3/2}\cdot\frac{1}{9\sqrt{30}}\cdot\frac{4r^2}{9a_0^2}.\mathrm{e}^{-\frac{r}{3a_0}}$	0	$\sqrt{\frac{5}{16\pi}}.(3\cos^2\theta-1)$	$3\,d_{z^2}$

IV.8.3. Graphical representations of atomic orbitals

In the case of an ns orbital, the volume corresponding to a maximum probability of presence is spherical. The wave function $\psi_{n00}, l = 0$, does not depend on θ or φ but it does depend on r. Its value is the same in all directions. The probability of presence is also independent of the direction, the orbitals will be spherical (Figure IV.16).

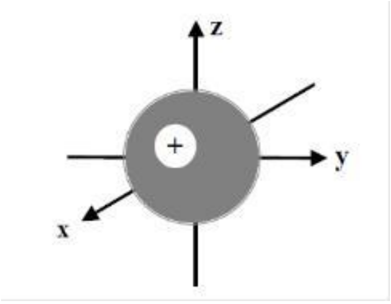


Figure IV.16: Graphical representation of the OA ns

The p orbitals (l = 1) can be represented by two roughly spherical lobes, joined together, having as axes of symmetry the x, y and z axes of the reference trihedron. They are therefore called "n px", "n py " and "n pz" depending on the value of m_l (n≥2) (Figure IV.17).

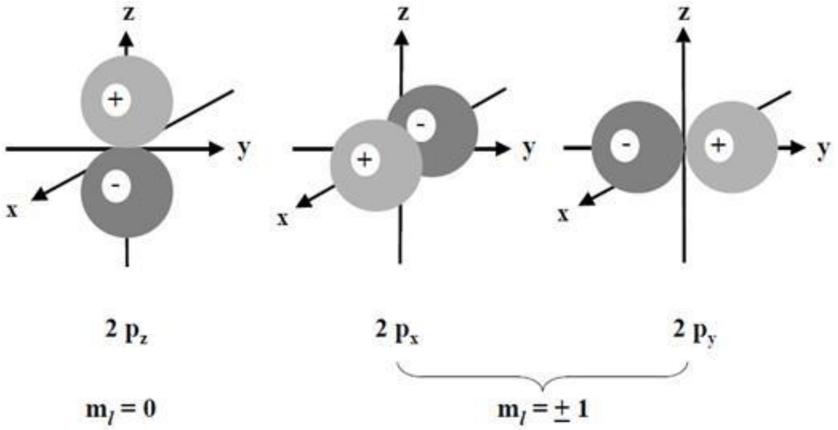


Figure IV.17: Graphical representation of the OA np , the + and – signs indicate the sign of ψ.

In the case of nd orbitals , the wave function depends on the angular quantities Θ(θ), Φ(φ). The probability of presence takes different values depending on the direction. The symmetry of these orbitals is no longer spherical. To represent this geometric shape, we use the square of their angular part. We then obtain a lobe-shaped envelope. $l = 2 \Rightarrow m_l = -2, -1, 0, 1, 2$ (n≥3) (Figure IV.18).

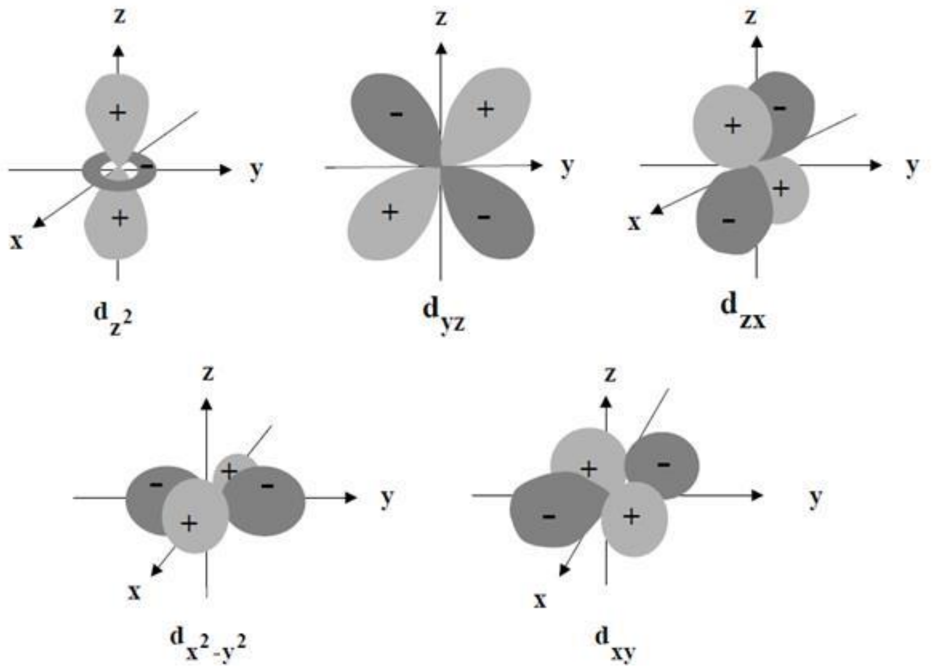


Figure IV.18: Graphical representation of the OA nd , the + and – signs indicate the sign of ψ.

Application exercises

Exercise 1

1. Using the relationships between the three quantum numbers n, l and m, determine the number of orbitals in the first three energy levels of the hydrogen atom.

2. Show that the maximum number of electrons that can be contained in the shell of quantum number **n** is equal to $\mathbf{2n^2}$.

3. Give the usual designation of the following orbitals: $\Psi 3,0,0$; $\Psi 3,2,0$; $\Psi 2,1,-1$.

Solution

1. Each orbital is designated by the term Ψ nlm as shown in the following table

Energy Level (n)	Angular Momentum Quantum Number (l)	Magnetic Quantum Number (m)	Orbital	Common Notation	Approximate Shape
1	0	0	$\Psi_{1,0,0}$	1s	Spherical
2	0	0	$\Psi_{2,0,0}$	2s	Spherical (larger than 1s)
2	1	-1, 0, 1	$\Psi_{2,1,-1}$, $\Psi_{2,1,0}$, $\Psi_{2,1,1}$	$2p_x$, $2p_\gamma$, $2p_2$	Dumbbell
3	0	0	$\Psi_{3,0,0}$	3s	Spherical (larger than 2s)
3	1	-1, 0, 1	$\Psi_{3,1,-1}$, $\Psi_{3,1,0}$, $\Psi_{3,1,1}$	$3p_x$, $3p_\gamma$, $3p_2$	Dumbbell (larger than 2p)
3	2	-2, -1, 0, 1, 2	$\Psi_{3,2,-2}$, $\Psi_{3,2,-1}$, $\Psi_{3,2,0}$, $\Psi_{3,2,1}$, $\Psi_{3,2,2}$	3d	Complex shapes (cloverleaf, donut)

2. the maximum number of electrons that can be contained in the shell of quantum number n:

In the n = 1 shell we have an atomic orbital (AO) => $n^2 = 1$

In the n = 2 shell we have four atomic orbitals => $n^2 = 4$

In the n = 3 shell we have nine atomic orbitals => $n^2 = 9$

The number of OAs for each value of n (or level) is n^2.

In each orbital we have two electrons at most. So the maximum number of electrons that the quantum number shell can hold is equal to $2n^2$. (This is no longer valid for n>4).

3. The wave function **(** or orbital) is determined by three numbers

quantum n, l and m.

$\Psi_{3,0,0} \Rightarrow \Psi_{n,l,m} \Rightarrow$ n = 3, l = 0 (s orbital) and m = 0 => 3s orbital

$\Psi_{3,2,0}$ => $\Psi_{n,l,m}$ => n = 3, l = 2 (d orbital) and m = 0 => 3d orbital

$\Psi_{2,1,-1}$ => $\Psi_{n,l,m}$ => n = 2, l = 1 (p orbital) and m = -1 => 2p orbital

Polyelectronic atoms (Screening effect: Slater approximation)

Polyelectronic atoms such as helium (the simplest polyelectronic atom) have several interacting electrons in their electron shells. Therefore it is impossible to treat each electron independently of the others. Indeed the potential to which an electron is subjected depends on the positions of all the other electrons. It is therefore necessary to solve the Schrödinger equation for all the electrons at the same time. For an atom with k electrons the expression of the Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{\mathrm{k}}\nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0}.\left(\sum_{i=1}^{\mathrm{k}}\frac{-\mathrm{Z}}{r_i} + \sum_{j=1}^{\mathrm{k}}\sum_{i=1}^{\mathrm{k}}\frac{1}{r_{ij}}\right)$$

r $_i$ denotes the distance between the nucleus and $^{\text{the}}$ ith electron, r $_{ij}$ denotes the distance between the i $^{\text{th}}$ and I electrons

multi-electron $\psi(r_1, r_2, r_3, r_k)$wave functions . This problem is complex to solve analytically, so we have to make approximations.

The usual approximation is to write the multi-electronic wave function as a product of mono-electronic wave functions

$$\psi(r_1, r_2, \dots, r_k) = \psi_1(r_1)\psi_2(r_2)\dots\psi_k(r_k)$$

We then have a system of k equations:

$$\widehat{H_i}\psi_i = E_i\psi_i$$

The total energy is the sum of the E_i :

$$E = \sum_{i=1}^{k} E_i$$

The problem in solving this system is to determine the different Hamiltonians , that is, to determine the potential energy field for the different electrons.

In 1930 John Slater published a model that considered each electron as being subjected only to a central potential from the nucleus. The electrons in the lower layers have an influence on the potential felt by the electron, because they act as a screen between the nucleus and the electron in question. The latter no longer sees a charge Ze , but a lower $Z_i^* e$charge .

Slater states the following rules of thumb:

1) We first establish the electronic configuration by ordering the OAs by increasing values of n, then we divide the OAs into several groups:

(1s); (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d); (4f); (5s, 5p); (5d) ...

2) The screening constant σ_i of the electron occupying the OA is obtained by adding the screening factors $\sigma_{j\to i}$ reflecting the screening exerted by the other electrons. The screening factors $\sigma_{j\to i}$ are calculated with the following conventions:

• For an electron occupying a 1s OA, the screening created by the other 1s electron corresponds to a screening factor $\sigma_{j\to i}$ equal to 0.30.

• For an electron occupying an ns or np OA , the screening created by an electron located in an OA of principal quantum number n' corresponds to a screening factor $\sigma_{j\to i}$ such that:

$\sigma_{j\to i} = 1$ if $n' < n - 1$ (total screening)

$\sigma_{j\to i} = 0.85$ if $n' = n - 1$ (large screening)

$\sigma_{j\to i} = 0.35$ if $n' = n$ (weak screening)

$\sigma_{j\to i} = 0$ if $n' > n$ (zero screening)

• For an electron occupying an OA nd or nf , the screening created by an electron of the same group corresponds to a screening factor $\sigma_{j\to i} = 0.35$, and to a screening factor $\sigma_{j\to i} = 1$ for all electrons located in lower groups.

The table shows the values of the coefficients $\sigma_{\iota\varphi}$ exerted on electron j by electron i.

In the Slater approximation, the attraction between the Zth electron of the atom and the nucleus is considered to be subject to the action of a nucleus whose charge number is no longer that of Z protons. The charge of the nucleus of the atom then becomes an effective charge Z*. This charge, which is weaker than the real charge of the nucleus, is obtained by subtracting the screening effects of the other electrons from the real Z:

$$Z_j^* = Z - \sigma_j \; avec \; \sigma_j = \sum_i \sigma_{ij}$$

σij : screening constant for each electron i that exerts a screening effect on an electron j (Table IV.4)

σj , screen constant

This formula is called Slater's mono-electron attraction and depends on the position of the (Z-1) th electrons of the atom relative to the ^{Zth} electron j.

Table IV.4: values of the coefficients $\sigma_{\iota\varphi}$ exerted on electron j by an electron i.

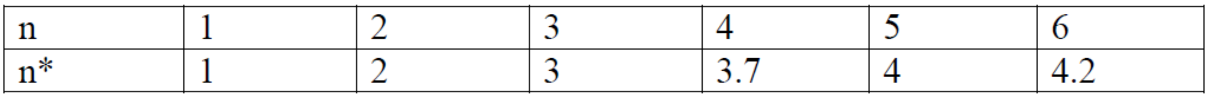
Electron Considered	**Screening Electrons**					
	(1s)	**(2s, 2p)**	**(3s, 3p)**	**(3d)**	**(4s, 4p)**	**(4d)**
1s	**0.30**					
2s, 2p	**0.85**	**0.35**				
3s, 3p	**1**	**0.85**	**0.35**			
3d	**1**	**1**	**1**	**0.35**		
4s, 4p	**1**	**1**	**0.85**	**0.85**	**0.35**	
4d	**1**	**1**	**1**	**1**	**1**	**0.35**
4f	**1**	**1**	**1**	**1**	**1**	**1**

The energy of $^{\text{the}}$ jth electron is calculated by the following relation: $E_j = \frac{-13,6*Z^{*2}}{n^{*2}}$

The radius between the atom and this electron equals $r = \frac{0,53*n^{*2}}{Z^*}$

n * = apparent quantum number introduced by Slater to reduce the differences between experimental and calculated values (Table IV.5).

Table IV.5: Apparent quantum number values for each principal quantum number value n ..



n	1	2	3	4	5	6
n*	1	2	3	3.7	4	4.2

In the Slater approximation, the energy E of an atom is equal to the sum of the energies of the electrons of the different electron groups:

$$E = \sum n_j E_j$$

Example

Calculate the effective charge and energy of an outer electron of the chlorine atom Z=17.

Solution

The effective nuclear charge can be calculated based on the figure below

$Z^* = 17-(2x1)-(8x0.85) -(6x0.35)=6.1$

His energy

$$E_3 = \frac{-13,6 * Z^{*2}}{n^{*2}} = \frac{-13,6 * 6,1^2}{3^2} = -56,22 \text{ eV}$$

IV. 10. Electronic configuration

To give the electronic configuration (or electronic structure) of an atom is to specify the distribution of electrons in the various layers and sub-layers of this atom in the ground state. The rules to follow to achieve the electronic configuration are: the stability principle, the Klechkowski rule , the Pauli exclusion principle and the Hund rule .

IV.10.1. Principle of stability

When the atom is in the ground state, the electrons occupy the lowest energy levels, the capacity of each level equal to $2n^2$ ..

IV.10.2. Klechkowski rule

The order of filling the various layers and sub-layers is done by increasing values of the couple (n + l). The order of increasing energies of the orbitals is the order of increasing values of the sum (n + l).

If two or more pairs (n + l) lead to the same sum, they will be classified in order of increasing n. The order of filling of the atomic orbitals is done according to the Klechkowski rule :

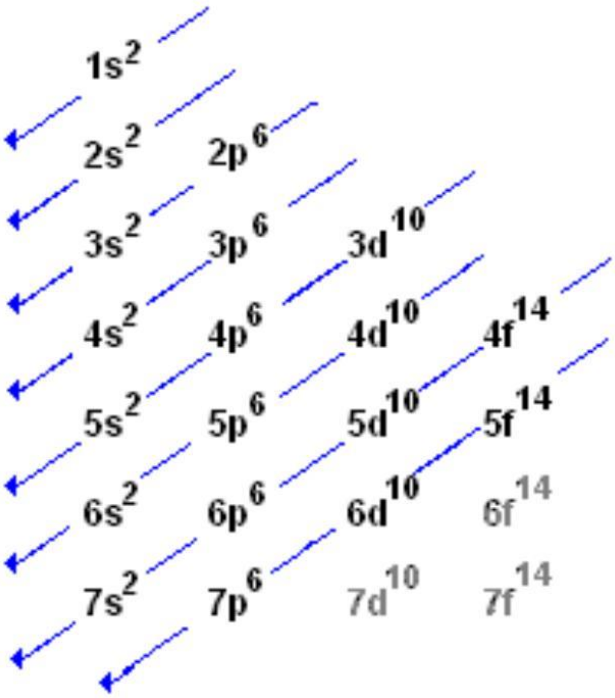


Figure IV.19: Explanatory diagram of the electronic configuration according to the method of Klechkowski

Reading is then done along the columns. We therefore find the following filling order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,

The outermost layer of the atom fixes the chemical properties, for this reason this layer is the most important and is called the valence layer of the atom. The other more internal layers are called nucleus layers and generally do not need to be detailed.

Often, and to make only the valence layer appear, the internal layers are replaced by the electronic configuration of the closest rare gas.

He for $2 < Z < 10$

Not for $10 < Z < 18$

Ar for $18 < Z < 36$

Kr for $36 < Z < 54$

Xe for $54 < Z < 86$

Rn for $Z > 86$

Ex: for iodine $Z = 53$:$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $5s^2$, $5p^5$

We know that the configuration of Krypton (Kr) is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$,$4s^2$, $4p^6$, $4d^{10}$

So we can write more simply I(Z=53): (Kr) $4d^{10}$, $5s^2$, $5p^5$

Exceptions to Klechkowski 's Rule

Some transition metals as well as some lanthanides and actinides do not respect the Klechkowski rule . We then observe a transfer between their s subshell (for transition metals) or f (for lanthanides and actinides) to the benefit of their d subshell which allows the latter to be filled. Generally, the exceptions are found when the electronic configurations are of the type:

$(n-1)d^4 ns^2$ replaced by $(n-1)d^5 ns^1$ (example $_{24}$Cr: [Ar]$4s^2 3d^4$ becomes $_{24}$Cr: [Ar]$4s^1 3d^5$)

$(n-1)d^9 ns^2$ replaced by $(n-1)d^{10} ns^1$ (example $_{29}$Cu: [Ar]$4s^2 3d^9$ becomes $_{29}$Cu: [Ar]$4s^1 3d^{10}$)

$(n-1)f^2 nd^0$ replaced by $(n-1)f^1 nd^1$ (example Ce: [Xe] $6s^2 4f^2 4d^0$ becomes This: [Xe] $6s^2 5d^1 4f^1$.

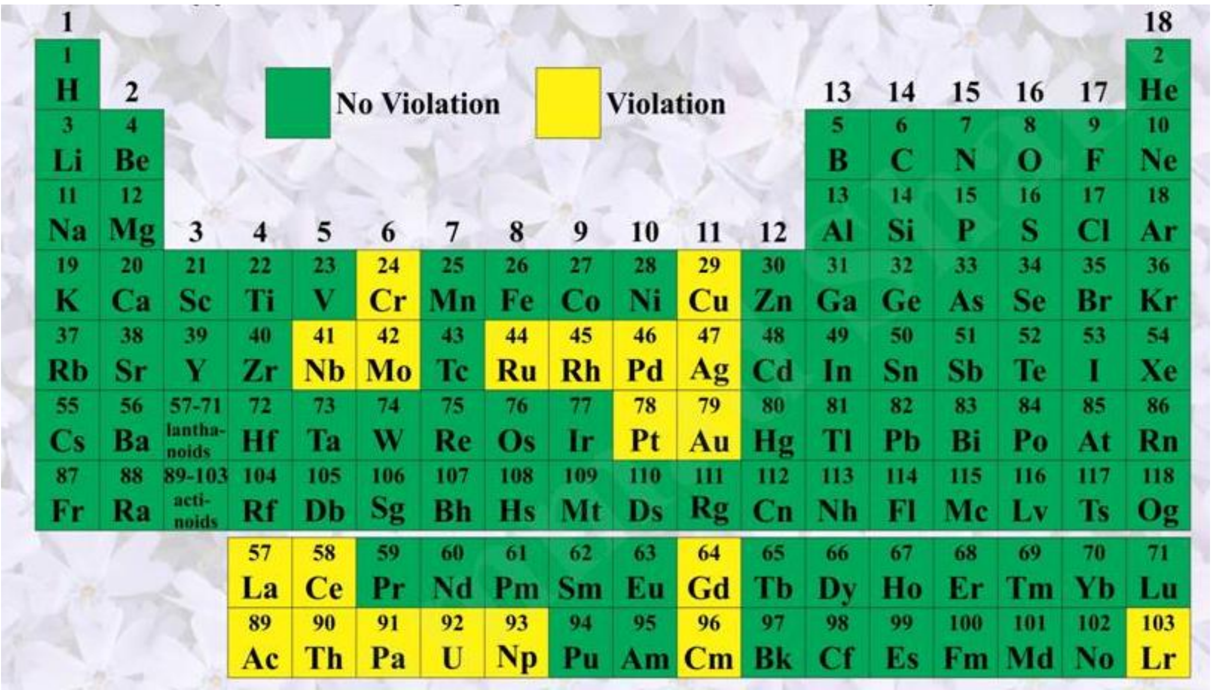


Figure IV.19 Elements that are exceptions to Klechkowski 's rule

IV.10.3. Exclusion of Pauli

The Pauli exclusion principle is a statement that two electrons in an atom cannot be in the same state at the same time (they do not have the same configuration). In other words; two electrons in the same atom cannot have the same four quantum numbers.

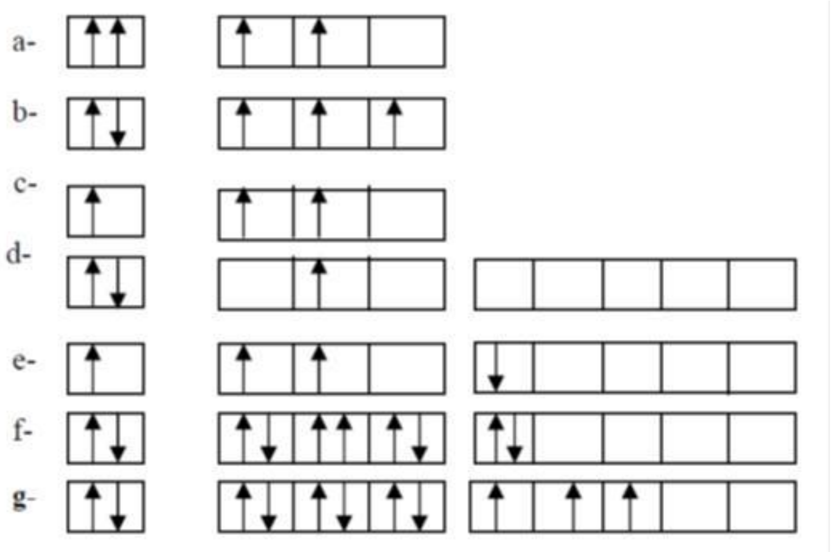
IV.10.4. Hund 's Rule

for a given subshell , the lowest energy electronic configuration is obtained by placing a maximum of electrons of the same spin (same ms value) in different orbitals, before pairing electrons of opposite spins (opposite ms values).

Application exercises

Exercises 1

Among the following electronic structures, which ones do not respect the filling rules? Explain



Solution

a) Inexact state: the two spins must be opposite (Pauli rule).

b) Ground state

c) Excited state

d) Ground state

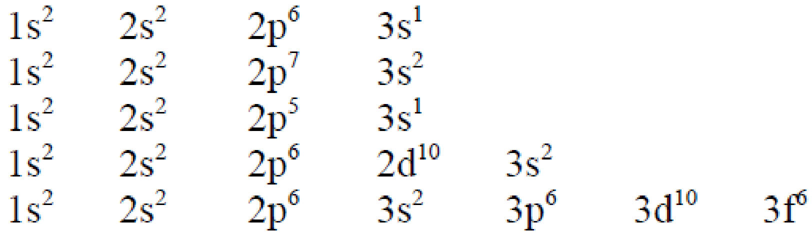
e) Excited state

Hund 's rule and Pauli principle are not

g) Ground state

Exercise 2

Let the following electronic structures be



$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^1$
$1s^2 \quad 2s^2 \quad 2p^7 \quad 3s^2$
$1s^2 \quad 2s^2 \quad 2p^5 \quad 3s^1$
$1s^2 \quad 2s^2 \quad 2p^6 \quad 2d^{10} \quad 3s^2$
$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 3d^{10} \quad 3f^6$

Which of these structures are in the ground state, which are in the excited state, and which are inexact.

Solution

$1s^2 2s^2 2p^6 3s^1$ Ground state

$1s^2 2s^2 2p^7 3s^2$ Inexact state (6 electrons maximum on p)

$1s^2 2s^2 2p^5 3s^1$ State excited

$1s^2 2s^2 2p^6 2d^{10} 3s^2$ Inexact state (no d orbital for n=2)

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 3f^6$ Inexact state (no f orbital for n=3)

Exercise 3

What is the number of valence electrons in vanadium V (Z=23) and gallium Ga (Z=31)? Give the four quantum numbers of these valence electrons.

Solution

For transition elements, valence electrons occupy the last shell and the subshell **being** filled.

- For vanadium, there are five valence electrons (s-type and d-type)

V (Z=23) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ (according to Klechkowski 's rule)

3d corresponds to $n = 3$, $l = 2$ $m = -2,-1, 0, 1,2$ $ms = + 1/2$

4s corresponds to $n = 4$ $l = 0$ $m = 0$ $ms = \pm 1/2$

- For gallium, there are three valence electrons (s-type and p-type)

Ga (Z = 31) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

4s corresponds to n = 4, l = 0 m = 0 ms = ±1/2

4p corresponds to n = 4, l = 1 m = -1, 0, 1 ms = +1/2

V. Periodic table of elements

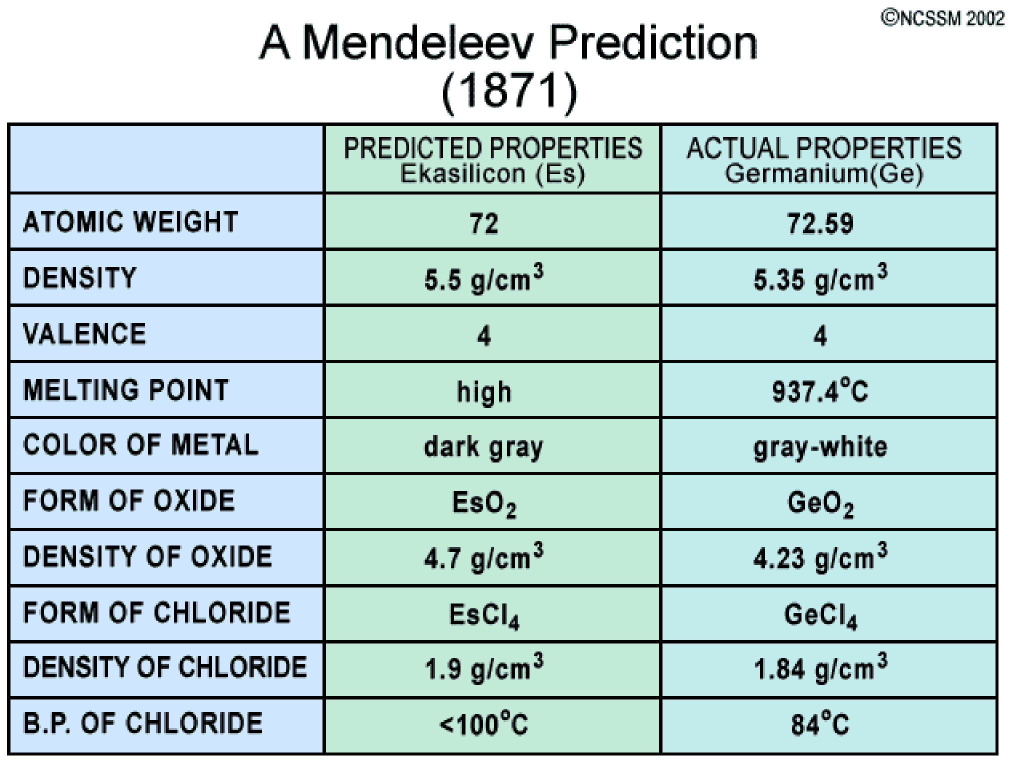
The periodic table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday resource for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random group of entities but display trends and are found together in families. A familiarity with the periodic table is essential for anyone who wishes to unravel the world and see how it is put together.

V.1. Periodic Table of D. Mendeleev

The periodic table as we know it today owes its development to the Russian chemist, Dmitri Mendeleev (1834 to 1907) and the German chemist, Lothar Meyer (1830 to 1895). Working independently, the two chemists in 1869 classified the chemical elements in ascending order according to their atomic masses, they observed a similarity in the physical and chemical properties of the elements at regular intervals. Mendeleev classified the elements horizontally and vertically in a table, whose elements are arranged in order of increasing atomic mass so that elements with similar properties occupy the same vertical column or in groups. Unfortunately, Mendeleev's method of classifying the elements seems more elaborate than that of Lothar Meyer.

Mendeleev predicted four chemical elements unknown at that time: eka -boron (Eb), eka -aluminium (Ea), eka -manganese (Em) and eka -silicon (Es). These elements are in good agreement with later discovered elements: scandium, gallium, technetium and germanium respectively (Table V.1).

Table V.1: Elements predicted by Mendeleev



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A Mendeleev Prediction
(1871)

	PREDICTED PROPERTIES Ekasilicon (Es)	ACTUAL PROPERTIES Germanium(Ge)
ATOMIC WEIGHT	72	72.59
DENSITY	5.5 g/cm^3	5.35 g/cm^3
VALENCE	4	4
MELTING POINT	high	937.4°C
COLOR OF METAL	dark gray	gray-white
FORM OF OXIDE	EsO_2	GeO_2
DENSITY OF OXIDE	4.7 g/cm^3	4.23 g/cm^3
FORM OF CHLORIDE	$EsCl_4$	$GeCl_4$
DENSITY OF CHLORIDE	1.9 g/cm^3	1.84 g/cm^3
B.P. OF CHLORIDE	<100°C	84°C

V.2. Modern periodic classification

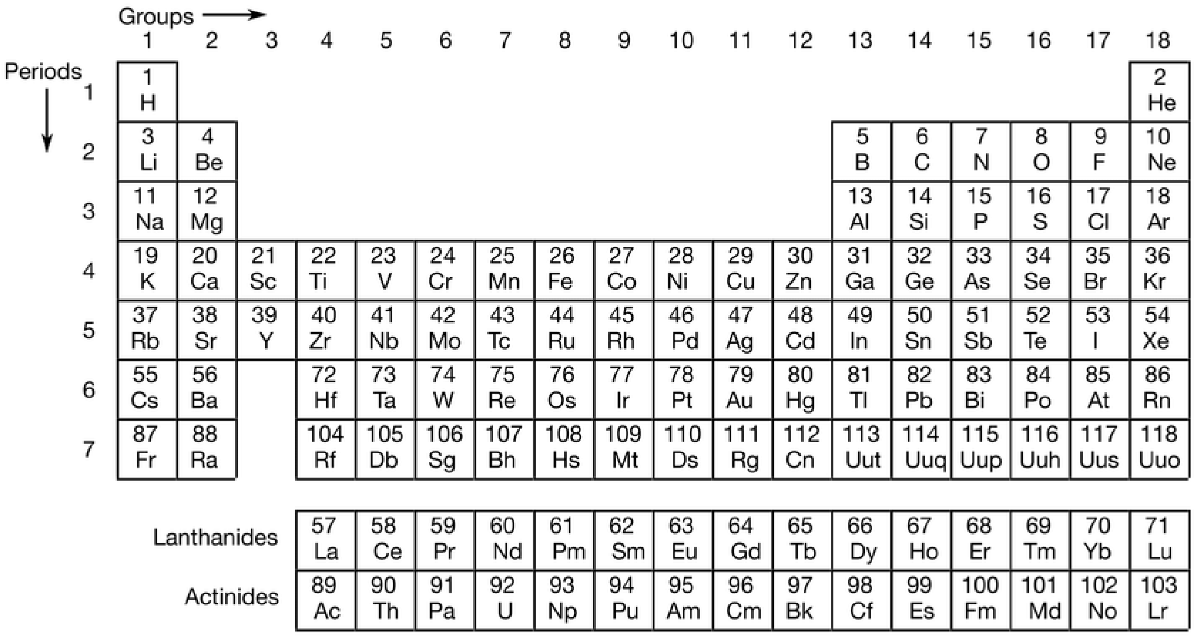
We must keep in mind that when Mendeleev developed his periodic table, chemists knew nothing about the internal structure of the atom. However, the early 20th century saw profound developments in theories about subatomic particles . In 1913, the English physicist, Henry Moseley observed linearity between the X-ray frequency and the atomic number. He thus showed that the atomic number is a more fundamental property of an element than its atomic mass. Mendeleev's periodic table was therefore modified accordingly and later called the modern periodic table. **The physical and chemical properties of the elements are periodic functions of their atomic numbers.**

The vertical columns are called **groups** (or families) and often have similar properties. According to the recommendation of the International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18, replacing the old group notation: IA…VIIA, IB…VIIB and 0; Some of these groups have special names:

  - Group 1 (Li, Na, K, Rb, Cs and Fr): the alkali metals.
  - Group 2 (Be, Mg, Ca, Sr, Ba and Ra): alkaline earth metals.
  - Group 15 (N, P, As, Sb and Bi): rarely called pnicogens .
  - Group 16 (O, S, Se, Te and Po): sometimes called the chalcogens .
  - Group 17 (F, Cl, Br , I and A): halogens.
  - Group 18 (He, Ne, Ar, Kr, Xe and Rn): the noble gases.
  - The block of elements between groups 2 and 13 is called the d-block or transition elements.
- The horizontal lines of the periodic table are called **periods** . A new period is used whenever the electron configuration of the atom involves a new value of the principal quantum number n. Period 1 consists only of the two elements H and He. Period 2 consists of the elements Li, Be, B, C, N, O, F, and Ne.
- Hydrogen really doesn't belong in any group of the periodic table, it's usually placed at the top.
- To keep the periodic table on one page, the lanthanides (elements 57-70) and actinides (elements 89-102) are usually written below the periodic table (Table V.2).
- All elements in a given group have the same number of electrons in the valence shell of their atoms.
- The chemical elements in the same column have the same valence electronic configuration; these elements constitute a chemical family and have similar chemical properties:
  - Elements of groups 1 and 2 are often called s-block elements, because their valence shell ends in the s-subshell.
  - Elements in groups 13 to 18 are often called p-block elements, because their valence shell ends in the p subshell.

- Elements in groups 2 through 13 are often called d-block or transition elements, because their valence shells end in the d subshell.
- The elements of the block f their layers end with the sublayer f . .

Table V.2: Modern periodic table



Periods \ Groups →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

V.3. Periodic properties of the elements

Once the electronic structure of atoms was elucidated, chemists quickly realized that the similar properties of the elements arose from their similar periodic electronic configurations.

V.3.1. The atomic radius

It has been seen that an atomic orbital does not have a precise boundary, for this reason scientists have found several possible approaches. One of the methods consists in measuring the distance separating the atoms in a sample of the element (for example Cl2, O2 and diamond), while half corresponds to the atomic radius (Figure V.1).

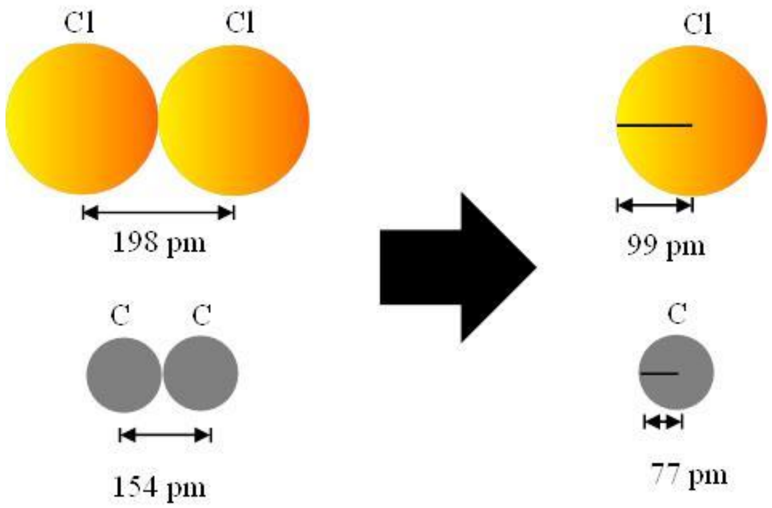


Figure V.1: Method of calculating the atomic radius

This method is applicable for atoms that form molecules, for metals their radii are estimated from their crystalline forms .

Generally speaking, atomic radii increase in a group from top to bottom and decrease in a period from left to right, this means two important things:

- The size of an atom is determined by its peripheral electrons. In a group the values of the principal quantum number n increase, the orbitals are more and more voluminous, the internal electrons occupy more and more space and the peripheral electrons must move further and further away from the nucleus: the size of the atoms increases;
- In a period the principal quantum number n of the peripheral electrons is identical for each element. From one element to another, a proton is added to the nucleus as a peripheral electron is added. The effect of the proton on the nucleus-electron interactions is greater compared to the effective charge, due to the addition of the electron, which increases a little. The attractive force applied to the electrons by the nucleus is large, this will be translated by a decrease in the atomic radius.

For an ion (atom whose charge has become positive or negative following the loss or capture of one or more electrons.

$$r_{cation} < r_{atome}$$

$$r_{anion} > r_{atome}$$

V.3.2. Ionization energy

Ionization energy is the energy required to remove an electron from an atom in the gaseous state, in its ground state.

$$M\ (g) \rightarrow\ M^{*}(g) + e^{-} \qquad E_i = E\ (M^{+}(\ g)) - E(M(g))$$

There are several ionization energies: the first ionization energy (often used) corresponds to the removal of a first electron from the atom in its fundamental state . The removal of a second and third electron corresponds to a second and third ionization energy respectively. Each time an electron is removed, a greater energy must be provided to extract the next electron, because the charge of the cation formed by each extraction increases gradually.

For example, magnesium has the following electronic structure: $1s^2 2s^2 2p^6$,$3s^2$ the removal of the two electrons from the s subshell, corresponds to the first and second ionization energy which leads to the formation of Mg^{+2} is feasible given the energy that must be provided 738 kJ/mol and 1451 kJ/mol respectively. On the other hand, it is very difficult to go and find the third electron, because it belongs to the p subshell and the energy that must be provided is significantly higher 7733 kJ/mol. Figure V.2 shows the evolution of the first ionization energy of the atoms of the different chemical elements according to their atomic number.

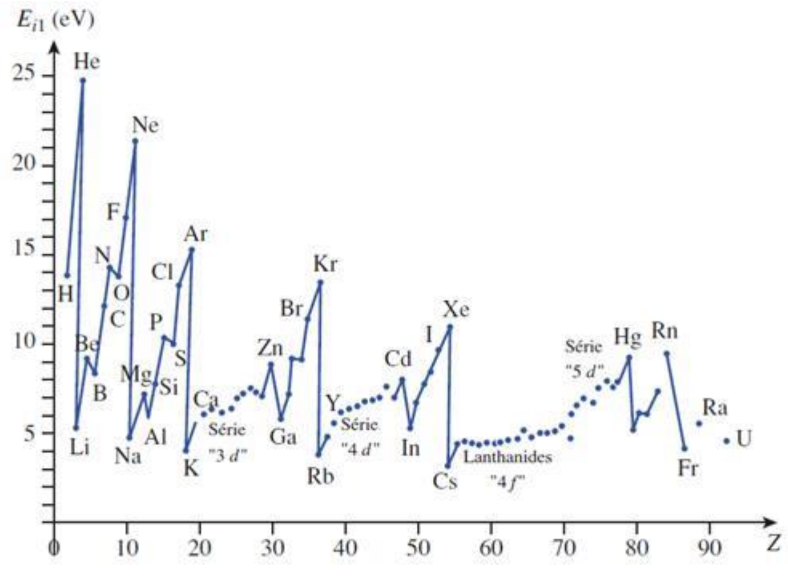


Figure V.2: First ionization energy of atoms as a function of their atomic number.

The first ionization energies of the s- and p-block elements of the table decrease within a group and generally increase within a period .

The decrease in the first ionization energy as we go down a column of the classification shows that the torn electron, which always occupies the same type of subshell within a column, is less and less bound to the nucleus. The energy of the valence subshell involved is therefore less and less low as its principal quantum number increases.

The direction of evolution within a period includes irregularities. The irregularity, which always exists between the elements of columns 2 and those of columns 13 (passage from the s block to the p block) corresponds to the fact that ionization results from the departure of an electron from an ns subshell for the former and from an np subshell , energetically less stable, for the latter.

Another anomaly occurs between the elements of column 15 and those of column 16. It can be interpreted by the particular stabilization of the half-filled subshells. It is therefore necessary to provide less energy to tear off an external electron from the oxygen atom than from the nitrogen atom.

V.3.3. Attachment energy and electronic affinity

The first electron attachment energy of an atom M is the energy E_{att} used to provide this gaseous atom with an additional electron according to the process:

$M\ (g) +\ e^{-}\ \rightarrow\ M^{-}(g)$ $\qquad E_{att} = E\ (M^{-}(g)) - E\ (\ M(\ g))$

Electron affinity is equal to the energy required to remove an electron from the gaseous M^{-} anion . $\qquad AE = -\ E_{att}$

The elements of highest AE are found at the top right of the table. In general, AE tends to ↗ from left to right, but many irregularities are observed (Figure.3).

<u>Examples of irregularities</u>

- The alkalis (ns1) seek to saturate their s subshell to give the ns2 structure (more stable), although located on the left in the periodic table, they then have AE > 0.

- The elements of the nitrogen column (ns2 np3), they have a certain stability (half-filled subshell). Nitrogen although located on the right in the table has an AE < 0.

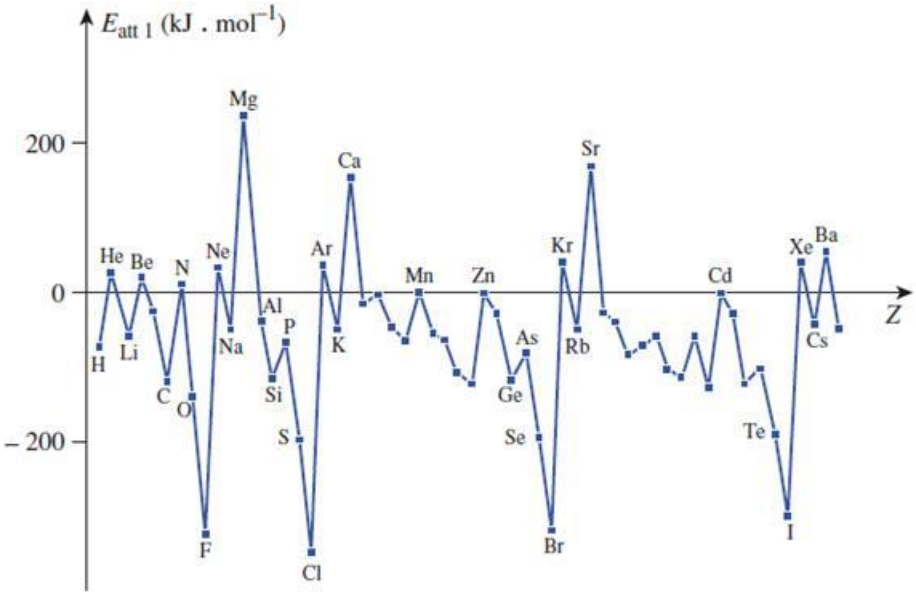


Figure V.3: First electron attachment energies E_{att} (kJ . mol $^{-1}$) of atoms as a function of their atomic number.

V.3.4. Electronegativity "EN".

It is a quantity which measures the ability of an element to attract electrons towards itself within a covalent bond ⇒ appearance of partial charges.

$$\overset{+\delta}{A} \text{———} \overset{-\delta}{B}$$ (B est plus électronégatif que A)

Several methods have been proposed to determine this quantity:

- Mulliken scale.

The electronegativity of an element in the Mulliken scale is equal to the arithmetic mean of the first ionization energy, E_{I1}, and the electron affinity, AE.

$$EN = k_M \left(\frac{E_{I1} + AE}{2} \right)$$

Electronegativity is a dimensionless quantity, the constant kM is therefore expressed in eV $^{-1}$ if the first ionization energy Ei1 and the electron affinity AE are expressed in eV. Originally, R. MULLIKEN proposed $k_M = 1$ eV $^{-1}$

- Pauling scale.

It is based on the bond dissociation energies of simple diatomic molecules:

E_{AA} , E_{BB} and E_{AB} : energies in kJ.mol $^{-1}$ to break the AA, BB and AB bonds. The difference in electronegativity between elements B and A is given by:

$$\Delta_{\aleph AB} = 0.12\ x\ (E_{AB} - (E_{AA} - E_{BB})\ \ \frac{1}{2})\ \ ^{1/2}$$

Electronegativity increases as we move from left to right and from bottom to top of the periodic table.

Application exercises

Exercise 1

Let the following atoms be:

N (Z=7), K (Z=19), Sc (Z=21), Cr (Z=24), Mn (Z=25), Fe (Z=26),

Cu (Z=29), Zn (Z=30), Ag (Z=47), Au (Z=79)

1. Give the electronic configurations of the atoms. Present the valence electrons for each atom. Deduce the number of valence electrons.

2. Place these atoms in the periodic table and group them if possible by family or by period.

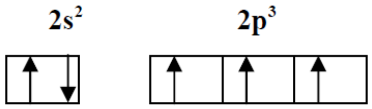
3. Cesium (Cs) belongs to the same family as potassium (K) and to the same period as gold (Au). Give its electronic configuration and atomic number.

Solution

1. We will write for each element, its electronic structure according to the Klechkowski rule and according to the spatial arrangement, and give the number valence electrons:

Example: N (7): $1s^2$ **$2s^2$ $2p^3$**

Representation of the valence shell using quantum boxes:



Element	Electron Configuration	Noble Gas Configuration	Number of Valence Electrons
N (7)	$1s^2 2s^2 2p^3$	[He] $2s^2 2p^3$	5
K (19)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	[Ar] $4s^1$	1
Sc (21)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	[Ar] $3d^1 4s^2$	3
Cr (24)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	[Ar] $3d^5 4s^1$	6
Mn (25)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	[Ar] $3d^5 4s^2$	7
Fe (26)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	[Ar] $3d^6 4s^2$	8
Cu (29)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	[Ar] $3d^{10} 4s^1$	11
Zn (30)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	[Ar] $3d^{10} 4s^2$	2
Ag (47)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1 4d^{10}$	[Kr] $4d^{10} 5s^1$	11
Au (79)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14} 5d^{10}$	[Xe] $4f^{14} 5d^{10} 6s^1$	11

Noticed :

In the case of chromium Cr (Z=24), the structure of the valence shell must be according to the Klechkowski rule : $4s^2 3d^4$. This structure is unstable. The most stable structure is therefore 4s1 3d5. The electronic structure of the 3d subshell is half filled.

In the case of copper Cu (Z=29), the structure of the valence layer must be according to the Klechkowski rule : $4s^2$ 3d9. This structure is unstable. The most stable structure is therefore $4s^1 3d^{10}$. The electronic structure of the 3d sublayer is completely filled. "Half-filled or completely filled d orbitals are more stable"

2. 2. Only one element belongs to the period n=2: N (Z=7) (group VA)

- The elements that belong to period n=4 are: K (group IA), Sc (group IIIB), Cr (group VIB), Mn (group VIIB), Fe (group VIIIB), Cu (group IB), Zn (group IIB)

- The elements that belong to the IB family are: Cu (4th period) Ag (5th period), Au (6th period)

- Elements that belong to the transition metal family (their valence shell is of type (n-1) dy nsx where l ≤ x≤ 2.and 1 ≤ y≤ 10) are: Sc (group IIIB), Cr (group VIB), Mn (group VIIB), Fe (group VIIIB), Cu (group IB), Zn (group IIB).

3. Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14}$ According to Klechkowski 's rule

$1s2\ 2s2\ 2p6\ 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} . 5s^2 . 5p^6 6s^1$ According to the spatial arrangement

The electronic structure of the cesium atom is:

[Xe] $6s^1$ and its atomic number is equal to 55 (Z=55).

Exercise 2.

Define the ionization energy, electron affinity and electronegativity of a

atom .

How do the atomic radius, electronegativity and ionization potential of elements vary according to a period and a column of the periodic table? Justify your answer.

Solution

Atomic radius:

In a column of the periodic table, as the period number (n) increases, the atomic radius increases.

In a period, n is constant, Z increases. The screening effect varies little, the electrons tend to be more attracted by the nucleus and consequently the radius decreases.

Ionization energy:

It is the energy required to supply an atom in its ground state (first ionization) or an ion (second or third ionization) to remove an electron from it. It decreases when the atomic radius increases and it increases when the radius decreases.

Electronic affinity:

it is the energy released (released in many cases) when an electron is captured by an atom to form an anion.

Electronegativity: This is the tendency of an atom to attract the electrons of the bond. It varies in the same direction as the ionization energy.

VI. Chemical bond

We have already seen that atoms of different elements react together to form compounds. The forces that hold these atoms together in compounds are called chemical bonds.

VI.1. Valence electrons

Valence electrons are those with the highest principal quantum number and those that belong to subshells that are being filled.

$$\text{Si: } 1s^2\,2s^2\,2p^6\,3s^2\,3p^2$$

Central electrons valence electrons

inner shells are filled, the central electrons are part of the inner electronic configuration. This can be used to write the following electronic configuration.

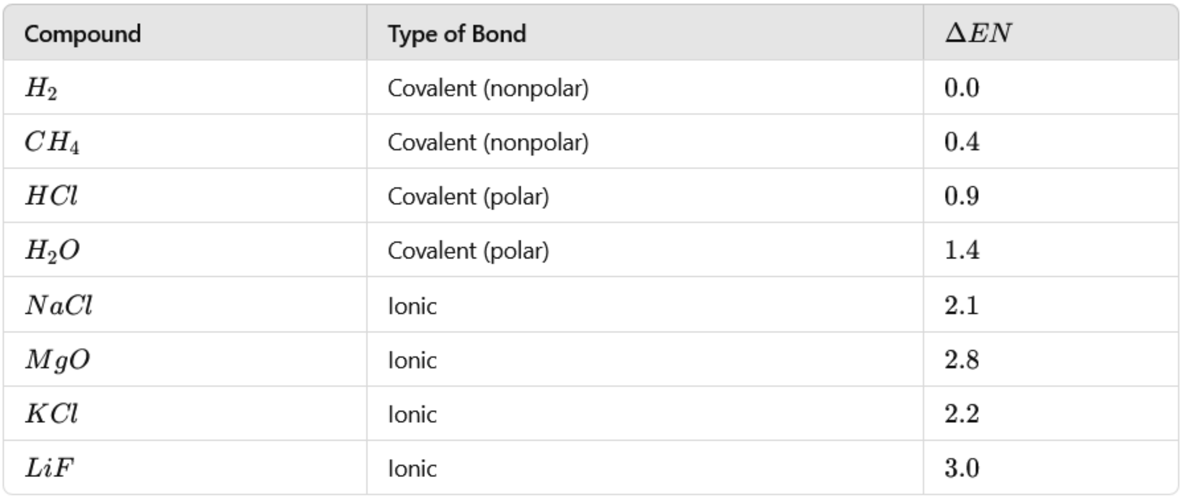
$$\text{Si: } \underline{1s^2\,2s^2\,2p^6} \quad 3s^2\,3p^2 \quad \Rightarrow \text{Si: [Ne] } 3s^2\,3p^2$$

Neon Config.

VI.2. Types of chemical bond

Valence electrons are most affected by the approach of another atom and are most likely to be involved in the formation of chemical bonds. The number of valence electrons determines how the chemical element will react. Chemical bonding determines the physical properties of substances, depending on the type of bond: covalent bond, ionic bond, and metallic bond.

The general rule is that a bond becomes ionic when the difference in electronegativity exceeds about 1.7, whereas a bond is covalent (often polar) for smaller differences.

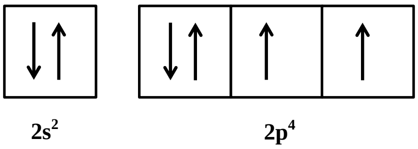


Compound	Type of Bond	ΔEN
H_2	Covalent (nonpolar)	0.0
CH_4	Covalent (nonpolar)	0.4
HCl	Covalent (polar)	0.9
H_2O	Covalent (polar)	1.4
$NaCl$	Ionic	2.1
MgO	Ionic	2.8
KCl	Ionic	2.2
LiF	Ionic	3.0

VI.2.1 The covalent bond

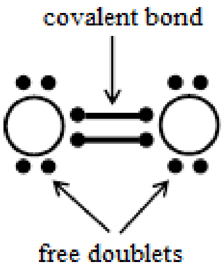
A covalent bond between two atoms A and B is formed when the mutual approach of the two atoms allows the overlap of the respective electronic clouds of the valence electrons and the pairing of the spins. **Lewis** was the first to propose in 1916 that a covalent bond results from a sharing of electrons: two, if the bond is single; four or six, respectively, if it is a double or triple bond. To construct the Lewis model, we will proceed in stages:

1. We write the electronic configuration of each atom constituting the molecule. For example O_2 : O (Z=8)$1s^2 2s^2 2p^4$
2. The number of electrons in the outer shell of each atom is given: 6 electrons occupy $2s^2 2p^4$.
3. To simplify, we can draw the valence shell in the form of quantum boxes



4. We count the possible covalent bond(s) between the atoms of the molecule: we have two free electrons in each atom (on the p layer) so they form a double bond.

5. We count the non-bonding doublets : on each atom we have two non-bonding doublets ($2s^2$ and one on the p layer).
6. All that remains is to distribute the covalent bonds between the atoms and place the non-bonding pairs around each atom:



VI.2.2. dative bond (coordination bond)

In a molecule AB, atom B has at least one electron pair (represented by a dash or two superimposed dots) and the other atom A has a vacant valence orbital corresponding to an electron gap (represented by an empty rectangle). Donor B provides one of its electron pairs to acceptor A, which then uses one of its free valence orbitals:

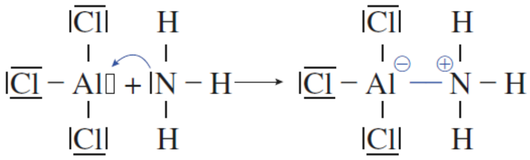
$$A\square \; + \; :B \longrightarrow \overset{-}{A}—\overset{+}{B}$$

The resulting A–B structure is globally uncharged because atoms A and B are initially uncharged. However, the sharing by B of its two electrons results in:

- for B by the formal loss of an electron and the appearance of a formal charge +e;
- for A by the formal gain of an electron and the appearance of a formal charge –e. Hence the notation:

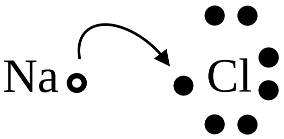
$$^{\ominus}A - B^{\oplus}$$

Such a bond is established during the reaction between aluminum chloride $AlCl3$ and ammonia $NH3$:

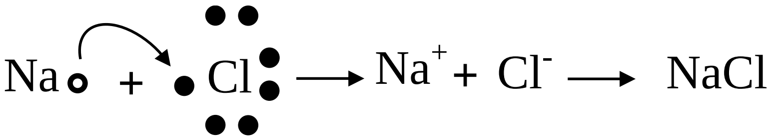


VI.2.3. Ionic bond

When a sodium atom reacts with a chlorine atom, the sodium chlorine salt is produced. The Lewis diagram of this molecule is as follows:



Sodium gives up its single electron to chlorine to have the stable electronic configuration of an inert gas (neon), while chlorine by gaining an electron reaches the stable configuration of argon.



VI.2.4. Metallic bond

When the bond involves elements located in the s, d or f blocks, Coulomb interactions persist but a different model must be used. All elements have a relatively marked electropositive character, especially for the s block. They tend to lose valence electrons and form cations; these electrons, which do not have a recipient of the halogen type (for example) constitute a negative set, the electron gas, free to move around the positive nuclei and ensuring the cohesion of the crystal. The bond is called metallic.

VI.3. Lewis diagram of molecules and molecular ions

VI.3.1. Obtaining the Lewis formula

1. From the electronic configurations of the atoms constituting the species considered, count the set Ne of valence electrons of this species:

N_e represents the sum of the N_v valence electrons of each atom.

q : represents the charge in the case of an ion ($q < 0$ for anions, $q > 0$ for cations)

$$N_e = \left(\sum N_V\right) - q$$

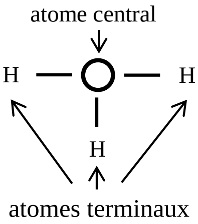
For example, the oxonium ion $H3O^+$: The hydrogen atom has one valence electron Nv (H) = 1, that of oxygen has six, Nv (O) = 6. The number of valence electrons to be taken into account is equal to : Ne = (3 x 1 + 6 x 1) – 1= 8

2. The number of electron doublets D to be distributed depends on the parity of N_e :$D = \frac{N_e}{2}$ doublets if N_e is even, $D = \frac{N_e - 1}{2}$ doublets if Ne is odd.

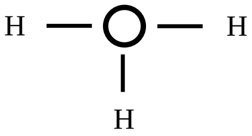
   We have, for H3O+, Ne is even this implies $D = \frac{8}{2} = 4$

   So we will have 4 doublets to distribute on the $H3O^+$ ion .

3. Arrange the chemical symbols of the atoms so that the terminal atoms surround the central atoms.

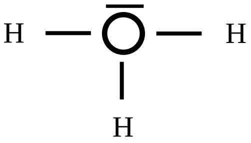


4. First use the doublets to form single bonds between the central atoms and each of their neighbors. Four doublets have been calculated for oxonium: the three bonds between O and H constitute the 3 doublets bound

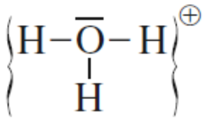


5. Complete the octet of each external atom by adding the necessary number of doublets (never for hydrogen, which is always monovalent).

6. Transfer all remaining doublets to the central atoms.

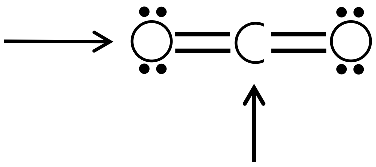


7. Assign the molecule its formal charge.



- *Octet Rule*

polyatomic ions to form structures in which eight electrons surround each atom except hydrogen is known as the octet rule.



Un octet autour de l'oxygène
(quatre électrons dans
la double liaison
et deux doublets libres

Un octet autour du carbone
(quatre électrons dans
Chacune des double liaison

VI.3.2. Species with formal charges

Many species have formal charges. To determine them, it is convenient to determine the number Na of valence electrons assigned to each atom of the structure by assuming the following rules:

• Any bonding pair is considered to be shared equally between the two atoms it binds.

• The electrons of a lone pair belong specifically to the atom on which it is located.

The calculation of Na is formal since the sharing of the bonded pair takes no account of the frequent difference in electronegativity $\Delta\ \chi = \chi\,(B) - \chi\,(A)$ which characterizes the two atoms.

Comparing this number N_a of electrons to the number N_v of real valence electrons of the atom gives the formal charge number z_F which characterizes it:

$z_F = N_v - N_a$

If $z_F = 0$, the formal charge is zero; any other value translates to:

– a defect of electrons if $z_F > 0$;

– an excess if $z_F < 0$.

The sum of the formal charges of the atoms constituting the chemical species considered is always equal to its overall electric charge, which can be translated as:

$\Sigma\ z_F = 0$ for a molecule

Example

Let us find the formal charges in Cl_3AlNH_3.

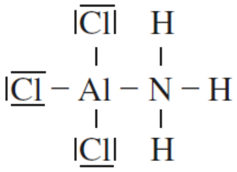
- The aluminum atom (Z = 13), with the electronic configuration in its ground state 1s2 2s2 2p63s2 3p1, has three valence electrons, Nv (Al) = 3.
- the chlorine atom (Z = 17), with the electronic configuration in its ground state 1s2 2s2 2p6 3s2 3p5, has seven, Nv (Cl) = 7,
- the nitrogen atom has five and the hydrogen atom has one.

Hence the number of valence electrons in the molecule to be taken into account:

Ne = 3 x 7 + 3 + 5 + 3 x 1 = 32

or sixteen doublets to place ($D = \frac{32}{2} = 16$).

Knowing the sequence of atoms, we first obtain:



In this structure, the aluminum atom has four bonding pairs, so we can assign it four valence electrons and a formal charge number $z_f = N_v - N_a = 3 - 4 = -1$.

the nitrogen atom also has four doublets, i.e.

$N_a = 4$ and $z_f = N_v - N_a = 5 - 4 = +1$.

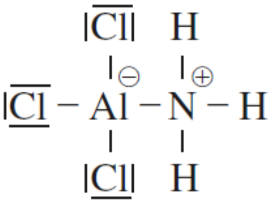
Chlorine atoms have three lone pairs and one bonding pair, i.e.

$N_v = N_a$ and $z_f = 0$.

Hydrogen atoms have a bonding pair, i.e.

$N_v = N_a$ and $z_f = 0$.

Lewis's representation of this building is deduced from this:



VI.4. The Polarized Covalent Bond

The bonding models we have just seen are, in reality, only borderline cases. A purely covalent bond, in which the doublet is shared equally, can only be established between two identical atoms located in the same environment. As soon as the bonded atoms are different, there is a strong chance that the sharing of the doublets is not equal. This results in a polar covalent bond in which the two atoms have a partial electric charge (Figure VI.1).

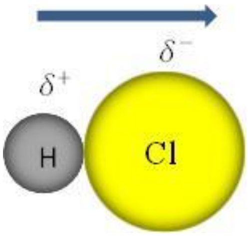


Figure VI.1: A polar covalent bond the electronegative atom receives a greater share of the bond pair.

In fact, the electron density will be shifted towards the most electronegative atom. The direction of polarization is given by partial charges (δ + for the least electronegative atom and δ - for the most electronegative). The greater the difference in electronegativity between the atoms, the higher the partial charges.

Dipole moment

The molecule is still globally neutral, since the number of electrons has not changed. But it has two poles, one positive, the other negative, it is polar. From an electronic point of view it is similar to a dipole, formed by the set of two charges + δ and – δ , at a distance d from one another. A dipole is characterized by its dipole moment μ (Figure VI.2).

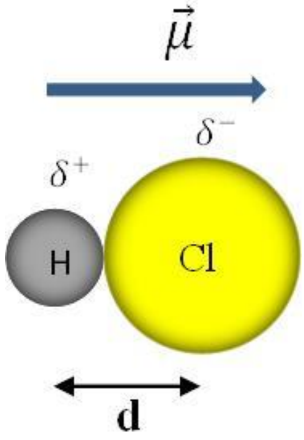


Figure VI.2: Representation of the dipole moment for HCl

This dipole moment μ is a vector quantity which has a direction and a modulus:

$$\|\vec{\mu}\| = \mu = \delta * d$$

μ= vector quantity having a direction, a sense and a module

q = coulomb charge > 0

d = distance between charges in meters

The ionic character of a bond is obtained by the following relation:

$$Caractère\ ionique\ (\%) = \frac{\mu_{\text{expérimentale}}}{\mu_{\text{théorique}}}$$

$\mu_{\text{experimental}}$: It is a measurable value, often proposed in tables (Table VI.1).

Table VI.1: Experimental dipole moment of some molecules:

1 Debye (D) = 3.338×10 $^{-30}$ Cm (SI unit)

Substance	Dipole Moment (Debye)	Substance	Dipole Moment (Debye)
HCN	2.93	CH_3F	1.81
HCl	01.03	CH_3Cl	1.87
HBr	0.78	CH_3Br	1.80
HI	0.38	CH_3I	1.64
H_2O	1.85	C_2H_5Cl	02.05
H_2S	0.95	n-C_3H_7Cl	2.10
NH_3	1.49	i-C_3H_7Cl	2.15
SO_2	1.61	CHF_3	1.61
CO_2	0.00	CH_2=CHCl	1.58
CO	0.12	CH≡CCl	0.44
NO	0.16	CH_3COCH_3	2.85
KF	8.62	CH_3OH	1.69
KCl	10.48	C_2H_5OH	1.69
KBr	10.41	$C_2H_5NO_2$	04.08
LiH	5.883	CH_3NO_2	3.50
B_2H_6	0.00	$C_6H_5CH_3$	0.37
H_2O_2	2.20		

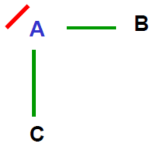
VI.5. Geometry of molecules: Gillespie theory or VSEPR

The VSEPR method allows, after analysis of the Lewis diagram, to predict the geometry of simple molecules or ions. It applies to molecules or ions. In 1957, the Canadian chemist RJ Gillespie developed the VSEPR model (Valence Shell Electron Pairs repulsion = repulsion of the electron pairs of the valence shell). It is not a new theory, but only a simple and effective reasoning process.

This model is based on the following rules:

1. All the doublets (bonding and free) of the valence shell of the central atom A are placed on the surface of a sphere centered on the nucleus.
2. The electron pairs are positioned so that the electronic repulsions are minimal (the pairs are located as far away from each other as possible).

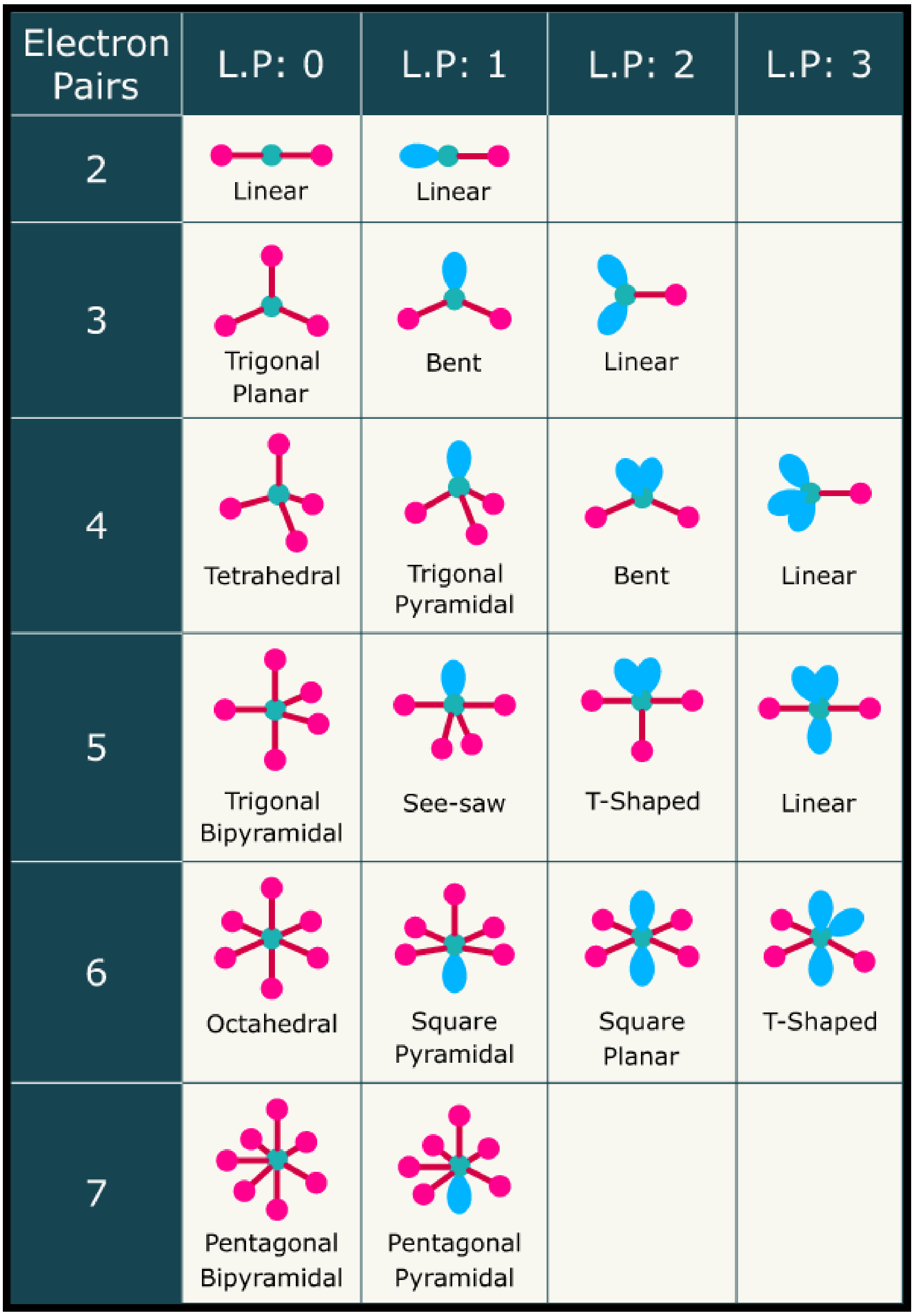
The molecule is symbolized by: AX_mE_n(A denotes the central atom which is linked to m X atoms and which has n pairs of free electrons or n non-bonding doublets). Knowing that the electronic doublets of the valence shell repel each other, the geometry of the whole will be that for which the repulsions are minimal, therefore the electronic doublets are as far apart as possible. We can then predict, from a Lewis diagram, the geometry of the molecule



It is therefore necessary to have established the Lewis representation of a structure before looking for the VSEPR formulation at the level of one of its atoms. Figure VI.3 and Table VI.2 give the geometries that can be predicted, as a first approximation, according to the VSEPR formulation. The position of the free doublets E, represented by a spindle, is well determined. These geometries are grouped according to the sum m + n coming from the formula AX_mE_n .

Table VI.2: Basic geometries for molecules of type $AX_m E_n$

m + n	**Basic Geometries**
2	linear
3	triangular plane
4	tetrahedral
5	trigonal bipyramid
6	octahedral



Electron Pairs	L.P: 0	L.P: 1	L.P: 2	L.P: 3
2	Linear	Linear		
3	Trigonal Planar	Bent	Linear	
4	Tetrahedral	Trigonal Pyramidal	Bent	Linear
5	Trigonal Bipyramidal	See-saw	T-Shaped	Linear
6	Octahedral	Square Pyramidal	Square Planar	T-Shaped
7	Pentagonal Bipyramidal	Pentagonal Pyramidal		

Figure VI.3. VSEPR formulas, corresponding geometries. Central atoms are shown in bold. Formulas for polyatomic structures involving only single bonds are written in black and those involving at least one multiple bond are written in blue.

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