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Faculty of Science and Technology

Department of Process Engineering

Polycopis

Cours

Mineral Chemistry

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FOREWORD

The course of mineral chemistry presented in this work, is addressed primarily to the students of the second year licence of engineering of the processes and second year licence chemistry.

We felt it was more than necessary to offer students in this cycle a complete course in inorganic chemistry, covering the study of the elements of the periodic table, their characteristics, the properties they share within the same family and the compounds they generate, as well as the types of bonding according to their state in nature or the conditions of their preparation reactions. The major industrial syntheses and metallurgies are presented.

This didactic work is primarily intended for students to help them understand the content of this speciality, which has applications in most aspects of the chemical industry, especially in materials science and environmental chemistry.

We hope that this handbook will be of use to students in process engineering, chemistry and other fields, and that it will serve as a useful reference too.

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Content of the matter

Pre-requisite knowledge: Basic knowledge of general chemistry

Chapter I

Reminder of some important definitions:

- Mole,
- Molar mass,
- Molar volume,
- Molar fraction,
- Mass fraction,
- Volume fraction ;
- Density ;
- Relationship between mass fraction and mole fraction;
- Material balance: Notion of reactant and reactant in excess,
- Notion of percentage excess,
- Notion of percentage of conversion

Chapter II

Crystallochemistry

Polyhedral description of structures, connectivity.

Chapter III

Periodicity and in-depth study of elemental properties

Halogens, Chalcogens, nitrogenand, phosphorus, boron.

Chapter IV

Major metallurgies

(Fe,Ti,Cu,Mg)

ChapterV

Major mineral syntheses :

- Sulfuric Acid H2SO4. Amonia NH_3
- Orthophosphoric Acid H_3PPO4

ChapterVI

Coordination Compounds, Ligands and Complexes, Stability of Complexes, Nomenclature of Complexes and Crystal Field Theory.

1 Table des matières

LIST OF FIGURES

LIST OF TABLES

Introduction:

Mineral chemistry is the chemistry of the bases which studies the atom the molecule the bonds between these particles the conductions of their formations …… etc. Mineral chemistry finds its application in all industrial or research fields.

For the details of this course, the statements of these parts are the subject of six (06) proposed chapters:

After a presentation of general notions about chemistry in the first chapter, in the second chapter It begins the presentation of the crystal bond, an ideal or real crystal, the detailed types of bonds: such as metallic, ionic and covalent bonding.

Chapter three is the periodic table with an explanation of the relationship between chemical families, their physical states in nature and their characteristics depending on whether they are metals or non-metals.

The fourth chapter is the halides and the electrolytic synthesis of the salts generated.

Chapter five covers chalcogens, oxides, and sulfur compounds, along with the industrial production method for sulfuric acid. Next, we explore the family of azides or pnictogens, with the procedures for synthesizing ammonia, nitric acid, and phosphoric acid.

Finally, in the sixth chapter, we give a detailed presentation on complexes and the bond between complex ligands….

1Chapter I Some Important Definitions

1.1 Mole

One mole corresponds to the quantity of matter in a system containing as many elementary entities as there are atoms in 12 g of carbon-12. One mole of atoms contains 6,022.1023 atoms. This number is called Avogadro's number after the Italian chemist who defined it.

`Avogadro Number:` **N** = 6.022 x 10^{+23} particles = One mole

1.2 Molar Volume

The molar volume of a gas is the volume that always occupies one mole of this gas under defined conditions of temperature and pressure.

- The symbol is Vm
- The unit is liter.mol-1 : l.mol-1

Under NTP conditions **Vm = 22.4 l.mol^{-1}**
Under STP conditions **Vm = 24.79 l.mol^{-1}**

Temperature and Pressure Conditions defined are:

1. Standard Temperature and Pressure Conditions **(CSTP)**

Vm = 22.4 l.mol^{-1}	T = 0°C P = 1 atm

2. Normal Conditions of Temperature and Pressure **(CNTP)**

Vm = 24.79 l.mol^{-1}	T = 25°C P = 1 bar

1.3 Mass density

The density of a solution is the mass of a unit volume of solution, at a given temperature.

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

$$\boxed{\mathbf{n} = \frac{m}{M} \quad ; \mathbf{n} = \frac{V}{\mathrm{Vm}} \quad ; \boldsymbol{\rho} = \frac{M}{V\mathrm{Vm}}}$$

1.4 Density

The density of a solution is equal to the ratio between the density of this solution and the density of water at 4°C. Since density is a ratio, density has no units.

$$\boxed{\mathrm{d} = \frac{\rho}{\rho_{(\mathrm{H20})}}}$$

Note

The density of pure water at 4°C is: d (H2O) = 1.000

1.5 Concentration units

Quantity of solute (dissolved substance) contained in a determined quantity of solvent or solution.

1.5.1 Mass fraction (w):

Mass of solute (usually expressed in g) contained in one gram of solution. The sum of the mass fractions (solvent and solutes) is 1.

1.5.2 Mass percentage (%):

Mass of solute (usually expressed in g) contained in 100 grams of solution. Usually when a chemist talks about percentage, he implies that it is % by mass.

1.5.3 Mass concentration :

Mass of solute (usually expressed in g) contained in 1 liter of solution. The unit is therefore: gram/liter (g/L).

1.5.4 Molar concentration:

Number of moles of solute contained in 1 liter of solution. The unit is therefore: mole/liter (mol/L).

1.5.5 Molality:

Number of moles of solute contained in 1 kilogram of solvent. The unit is therefore: mole/kilogram (mol/kg).

2 ChapterII

State of matter and crystal chemistry

Matter exists in three states: gaseous, liquid and solid. The form in which matter is found is determined by the interactions between its constituent particles (atoms, molecules or ions).

2.1. State of the matter

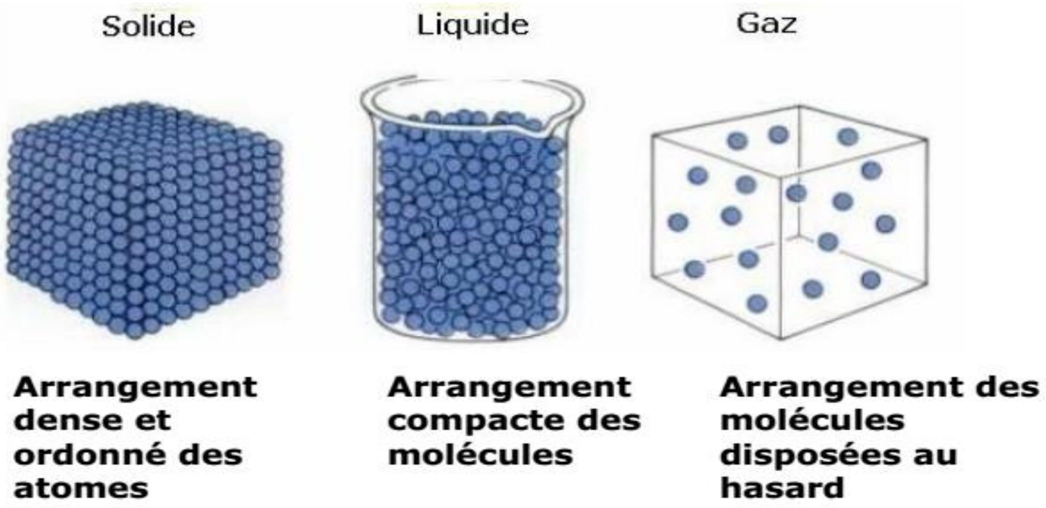


Figure 1 : Three State of Mater

The chemical entities we are surrounded by are molecules, or combinations of elements (atoms) of various nature and number. The elements combine to form molecules; it is created between the elements of the bonds of different forces.

The evolution of a system is an evolution tending not only towards a state of lower energy (enthalpic factor: ΔH°) but also towards a more probable state or state of greater disorder (entropic factor: ΔS°). In most chemical reactions there is a trade-off between enthalpic factor and entropic factor.

ΔG° (standard free energy variation) **$= \Delta H^\circ - T\Delta S^\circ$**

Every mechanical system tends towards a lower energy state. Two to several elements will combine together to form a MOLECULE, provided that the latter achieves a more stable chemical entity than the starting elements. Thermodynamic spontaneity is not the only factor to consider in order to explain the fate of a chemical reaction; it is also necessary that the reaction can be carried out at an appreciable (kinetic) speed.

The MOLECULE represents, on a microscopic scale, the smallest part of a body that could exist in the free state in nature while retaining all the characteristic properties of the original substance (cf. glossary). With rare exceptions, the molecule is a composite of at least two identical or different elements.

There are simple bodies = molecules made up of identical elements (e.g. H_2, N_2, O_2, F_2, Cl2,...) and compound bodies = molecules formed from elélements of different nature (H_2S, H_2O, CH_3COOH, ...).

2.1.1 Origin of Interatomic Bonds

All BONDS have a common origin: the electrostatic attraction between the positive charges of the atomic nucleus and the negative charges of the electrons.

There are attractions and repulsions between the electric charges of electrons and nuclei. The balance between this repulsive force and the electrostatic attraction force leads to a distance of equilibrium between two atoms, characteristic of the bond in question.

Electric charges of the same sign repel each other and electric charges of different sign attract each other.

Exemple : Na+ and Cl- form a sodium chloride crystal.

If there were no force (or extremely weak forces) between the atoms, there would be no molecule. This is what happens with rare gases (Ar, Kr, Xe, Ne), they do not combine with anything. And forces that develop between molecules give birth to a solid or liquid.

The interatomic bond energy is the energy that must be provided to break the bond. It is usually expressed in electron-volts (eV) per atom.

2.1.2 Type of links

Two types of links are distinguished:

- Chemical Bonds : They give birth to a new chemical entity. This bond is very strong (bonding energy), of several electrons Volt.
Ex: H (gas) and O (gas) give water H_2O (liquid).

Physical Bonds : They are forces but they develop between molecules. The result is a physical state (not a new chemical entity), leading to a variation in physical properties. These forces are small, a few tenths of eV.
Ex: 1- Water molecules at -10°C gather to form ice
2- Water (H2O) should be an ambient gas (like H2S, H2Se) or it is not. Why?

because forces develop between water molecules that do not exist between H2S and H2Se (hydrogen bond).

2.2 Chemical Bonds

2.2.1.1.1 Principle Byte rule

There are more advanced theories now but more abstract. So we will take the old model.

It was noticed that some gases (Ne, Ar, Kr, Xe) all have on their peripheral layer 8electrons and are chemically inert. And, in their various combinations, atoms tend to acquire the electronic configuration of the nearest rare gas, that is to say, having 8 electrons on their peripheral layer.

8 e- : inertia; < 8 e- : the molecule reacts. The atoms react to obtain these 8 electrons either by:

loss or gain of electrons: ionic bond,

Electron pooling: covalent bond. Intermediate cases (covalent + ionic) or metal bond.

2.2.1.1.2 The ionic bond

The ionic bond = strong metal + strong non-metal

The strongest metal, the strongest of all, is on the left and quite at the bottom of the periodic table: cesium. The strongest non-metal, the strongest of all, is to be found on the right and quite at the top: fluorine.

The ion bond is based on the effective transfer of one to more than one electron from the peripheral layer of the strong metal to the peripheral layer of the strong non-metal; the metal is potential donor of electron(s), the non-metal, acceptor.

An ionic combination is a combination of a cation and an anion, ions that are held in close proximity to each other, almost in contact, by coulomb-like attraction.

There are 3 types of force in the core. The first force is called strong interaction, it is a force of attraction that acts at very small distance (on the order of fentometer: 1.10-16m). The second is a repulsive force called coulomb interaction, that is to say it characterizes the repulsion/attraction between 2 identical/different electric charges.

The third is the low interaction force, which if the energy balance allows it, transforms a proton into a neutron and a positron.

Ex: Na has 8e- in total and 1e- on the peripheral layer, Cl has 7 e- on the peripheral layer. This gives the NaCl (sodium chloride, cooking salt). It is a very stable building, very compact (Figure 2)

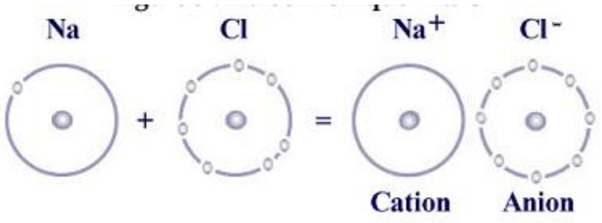


Figure 2 Ion bonding

2.2.1.1.3 The intermediate link

The two extreme types of bonding are ionic and covalent bonds. The most common binding model - and especially in organic chemistry- is intermediate between these two extremes: it is the polar or polarized or heterpolar covalent bond. It is partially covalent and partially ionic.

A covalent polaireresult of the pooling of electron(s) in a bilateral exchange of at least one electron from each of the 2 partners with a difference of electronegativity between 0.5 and 1.7.

Examples: HCl

- Hydrogen has 1 e- and Chlorine 7. H does not give its e- otherwise it no longer has. It makes available its e- and there is a joint venture of a doublet between hydrogen and chlorine. This doublet is not statistically in the middle, the probability of finding the doublet near chlorine is much higher. Hydrogen is highly positive. For NaCl (ionic bond), the probability is 100% around chlorine.

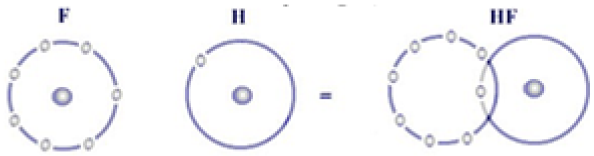


Figure 3 Polar covalent bond

Electronegativity:

This is the greater or lesser tendency of an atom to attract electrons into a molecular building. This causes some molecules to polarize. The molecule then behaves as a dipole, that is to say, as two opposite charges.

When one of the two atoms is much more electronegative than the other, the polarization of the molecule is so important that we are in the presence of two ions (ex: NaCl). It is as if sodium had lost its peripheral electron by becoming a positive ion Na+ and chlorine had gained this electron, by becoming a negative ion.

2.2.1.1.4 The metal bond

The metal bond concerns atoms with a small number of electrons on the outer layer, a situation encountered in the case of metals.

These electrons are weakly bound to the nucleus and can be easily removed from it. Atoms are then transformed into positive ions. The electrons removed from the atoms are put in common between all these atoms. They are an electronic “cloud” or “gas” that provides cohesion to the whole (Figure 5).

All these atoms have lost at least one electron. As the crystal is neutral (they remain in the crystal, they cannot leave it otherwise the crystal becomes positive and attracts the e^-).

The metal bond is therefore a set of ions +. Each charge + is surrounded by a charge -. The bond is very intense, several eV (about 5 eV).

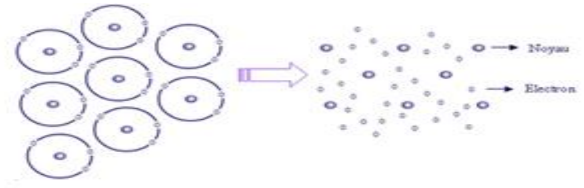


Figure 4:The metal bond

2.2.1.2 Physical Links

2.2.1.2.1 Van der Waals links

These are low-intensity interactions between atoms or molecules. These are electrical bonds like all bonds but they are physical bonds between molecules. Charges will repel and attract = Secondary bonds.

For a molecule, when we make the balance of positive charges and replace all these charges with a single charge = barycenter. That is—the point where everything happens as if all harges are put at this point. From an electrical point of view, when one is out of the molecule, everything happens as if these positive charges were at the barycenter of charges and everything happens as if the negative charges are at the barycenter of negative charges.

A molecule can therefore be represented by **: +q ---- −p**

with d, the distance between the 2 barycenters. From an electrical point of view, it is an electric dipole.

Exemple : Pullover is electrified because it appears dipoles. Polyvinyl discs attract dust (not magnetism).

Any molecule can be generally assimilated to an electric dipole (except spherical molecule). These dipoles will attract and repel each other. The existence of these dipoles will cause forces and orientation of molecules. A molecule will become a dipole in the presence of a dipolar molecule. All these forces are Van der Waals forces. They are weak but sufficient to create a liquid state.

2.2.1.2.2 The hydrogen bond

It is sometimes classified as chemical bonds but it does not create by a new state. When already joined to a first very electronegative element in a polarized covalent bond, any hydrogen can establish a second link with a very electronegative and small element:

Fluor or oxygen or nitrogen. This second link, symbolized by an interrupted trait, is called hydrogen bond or bridge. The term "bridge" meaning that it is a less strong bond than a covalence bond normal.

Ex: Carboxylic acid (R-COOH) : R -COOH……OH-C0R

The most well-known hydrogen bond is the bond between water molecules (H_2O):Oxygen being electronegative and hydrogen not being electronegative, there is a doublet pool but this doublet is more often close to oxygen than near hydrogen in other words statistically it is not located in the middle. Oxygen is negatively charged (small charge: -2q) and each hydrogen acquires a small charge (+1q). With another water molecule, the negative part will attract the positive part. Therefore, preferably around oxygen, there is another hydrogen atom. Between this charge -2q and this charge +1q, there will be a purely electrical attraction and it is the existence of this physical bond called hydrogen bond that makes the water molecules attract each other (what H_2Se and H_2S do not, which remain gases at t° ambient).

- Exemple :

$$\begin{array}{l} H-\overline{O}|\cdots H-O-H \\ \quad\;\; | \\ \quad\;\; H \end{array}$$

2.3 Crystallochemistry

2.3.1 General concepts

The solid is hard and does not deform. On the contrary, a liquid and a gas are deformed, they take the form of the container in which they are placed; The solid, placed regularly, forms crystals. In a crystal, there is an order.

- Liquids and gases are deformable (very low forces)
- Solids have their own shape and require considerable forces to form Solids can exist in two different states:

1- Disordered state characterized by an unordered structure is the case of amorphous systems, for example glasses.

2- An ordered state characterized by an orderly structure corresponds to crystalline solids.

2.3.2 Amorphous state

In the disordered state, the atoms or molecules constituting the matter are arranged essentially randomly. Gases and liquids of the old classification naturally belong to this category, but also amorphous solids such as glasses or certain polymers, which can actually be considered very high viscosity liquids. In the opposite, in the ordered or crystalline state), the constituent elements (atoms, ions or molecules) are distributed evenly along the three directions of space. These materials are sometimes qualified

2.3.3 Crystallised state

In the ordered or crystalline state, the constituent elements (atoms, ions or molecules) are distributed evenly along the three directions of space. These materials are sometimes referred to as “real solids”. Most of the objects around us fall into this category.

Single crystal or monocrystalline material: is a solid material made of a single crystal, formed from a single germ. In contrast, a polycrystal or polycrystalline material is made up of a multitude of small crystals of varying size and orientation.

On our scale, we have macrocrystals characterized by their characteristic geometric appearance: faces

2.3.3.1 The ideal or perfect crystal

The ideal or perfect crystal (the real crystal differs, but only slightly) consists of a regular arrangement of atoms, ions, or molecules in the three dimensions of space, and this regular arrangement of atoms extends practically to infinity.

At our scale, we observe macrocrystals characterized by their distinctive geometric appearance: flat faces, sharp edges, and well-defined angles between the faces (Figure N°6).

A crystal can be described using a mathematical entity, the lattice, and a material content, the motif. The "assembly" forms the crystal.

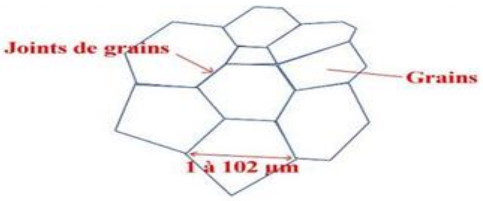


Figure 5: Structure of macro crystals of a metal

2.3.3.2 Real Crystal:

The real crystal differs from the perfect crystal due to its irregular distribution of atoms, ions, or molecules, as it contains defects (foreign particles) that penetrate the crystal structure.
Real crystals always contain a certain number of defects or singularities in varying quantities. The presence and quantity of defects depend on the type of chemical bond and the purity of the crystal.

2.3.4 Geometric Classification of Defects

Defects correspond to microscopic regions of a crystal where an atom is surrounded by nearby neighbors in positions different from those observed in a perfect crystal. Traditionally, defects are classified into four categories according to their dimensionality. The following paragraphs review point defects (0D), linear defects (1D), planar defects (2D), and volumetric defects (3D).

2.3.4.1 Point Defects:

Point defects are characterized by a disruption in the crystalline order limited to a crystallographic cell, typically:

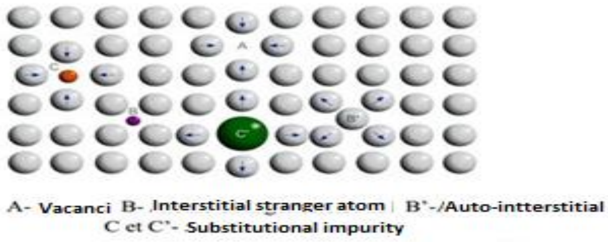


Figure 6: Point Defects

- Vacancies: These are empty spaces left in the structure at a site normally occupied by an atom.

- Interstitial atoms: These are excess atoms in a structure or impurities placed at sites that are normally vacant.
- Substitutional impurity: When an atom occupies a site normally held by an atom of a different chemical nature, it is referred to as a substitutional impurity.

2.3.4.2 Linear Defects

The linear defects observed in crystals are called dislocations (Figure 8). Dislocations occur when part of the crystal slides along a plane. The dislocation line itself corresponds to the line of the slip plane separating the part of the crystal that has moved from the part that has remained stationary. The slip vector **b** is known as the Burgers vector of the dislocation.

We distinguish between edge dislocations, where **b** is perpendicular to the dislocation line, and screw dislocations, where **b** is parallel to the dislocation line. Other dislocations are called mixed dislocated

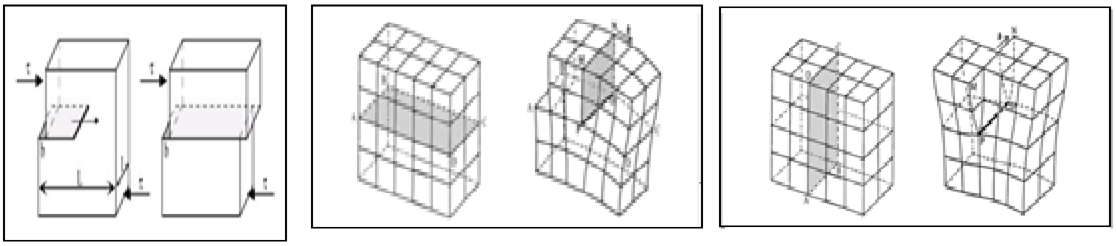


Figure 7 : An edge dislocation

2.3.4.3 Planar Defects

A planar defect corresponds to a disturbed region of the crystal, with a volume comparable to that of an atomic plane. Examples of planar defects include free surfaces that define a real crystalline sample, or grain boundaries, which are the boundary surfaces between crystallites in polycrystalline samples (Figure9a). Stacking faults are also common in compact etal structures (Figure 9b).

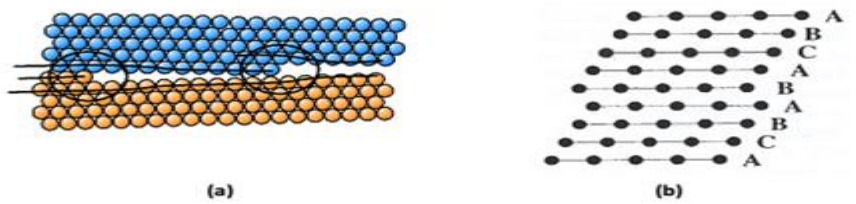


Figure 5: (a) Représentation schématique de l'arrangement des atomes au niveau d'un joint de grain dans un échantillon polycristallin. Le joint de grain, zone située entre deux cristallites adjacents, est un défaut qui correspond à la fois à une discontinuité d'orientation cristalline et à une zone dans laquelle les positions relatives des atomes ne correspondent pas aux positions d'équilibre minimisant le potentiel d'interaction. **(b)** Défaut d'empilement produit par l'absence d'un plan C dans la séquence ...ABC ABC A... constituant une structure cubique compacte. *Figure (b) extraite du livre « Bases physiques de la plasticité des solides », par J.-C. Tolédano.*

Figure 8: Planar Defects

These are regions of high disorder (with a thickness of a few interatomic distances) that separate crystals within a polycrystalline solid (Figure 6).

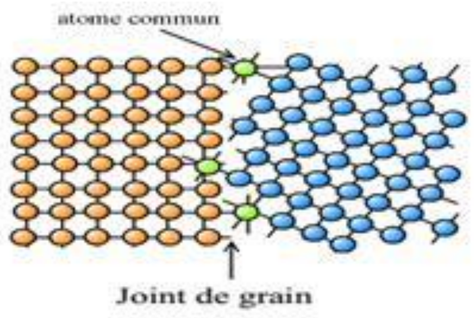


Figure 9: Grain boundaries

More often, crystalline materials are aggregates of numerous crystals, sometimes very small (from a few microns to several hundred microns). In these polycrystals, the ordered nature of the material at the scale of each crystal is no longer visible on a macroscopic level. Metals and metallic alloys fit this description. In the case of metals, the crystals in the aggregate are called **grains**, and the boundaries between these crystals are called **grain boundaries**.

The arrangement of atoms or groups of atoms in a crystalline solid, i.e., the overall crystal structure, depends on several factors, particularly the type of bond between atoms and the number of nearest neighbors, or coordination number, that each atom can accommodate.

2.3.5 Classification of Crystalline Solids

There are two types of crystalline solids:

2.3.5.1 Molecular crystals

Molecular crystals are formed by regular stacking of molecules; examples include iodine (I_2), carbon dioxide (CO_2), and water (H_2O).

2.3.5.2 Macromolecular crystals

In macromolecular crystals, the concept of a molecule as an independent chemical entity is replaced by the crystal itself, which acts as a molecule.

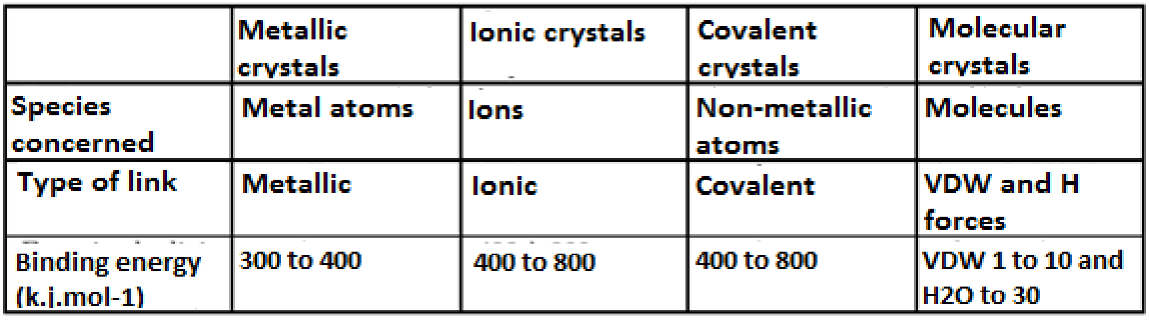
Among macromolecular crystals, we have:

1) Ionic crystals (e.g., NaCl, CsCl, CaF_2).

2) Covalent crystals (e.g., carbon in the forms of graphite and diamond, silicon, germanium).

3) Metallic crystals (e.g., sodium, iron, copper).

Tableau 1Classification of different types of crystals.



	Metallic crystals	Ionic crystals	Covalent crystals	Molecular crystals
Species concerned	Metal atoms	Ions	Non-metallic atoms	Molecules
Type of link	Metallic	Ionic	Covalent	VDW and H forces
Binding energy (k.j.mol-1)	300 to 400	400 to 800	400 to 800	VDW 1 to 10 and H2O to 30

2.3.6 Crystallography Concepts

The ideal or perfect crystal (the real crystal differs but only slightly) consists of a regular arrangement of atoms, ions, or molecules. A crystalline solid is made up of a large number of particles (ions, atoms, molecules) located at specific points in space

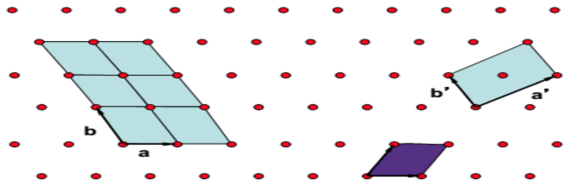
2.3.6.1 The Crystal Lattice

A periodic lattice consists of a set of identical patterns arranged periodically in one direction (one-dimensional lattice), in a plane (two-dimensional lattice), or in space (three-dimensional lattice). A crystal lattice is composed of a triply periodic arrangement of partic

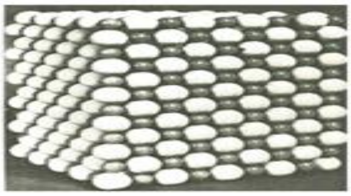
Exemple :

Monodimensional grid

Bidimensional grid



Tridimensional grid



The Crystal Unit Cell

The unit cell is defined as the simplest geometric structure that, by translation in the three spatial directions, allows the generation of the entire crystal lattice.

The unit cell is generally a parallelepiped, defined by three lengths and by three angles **(α, β, γ. a, b, and c)** are the unit cell parameters.

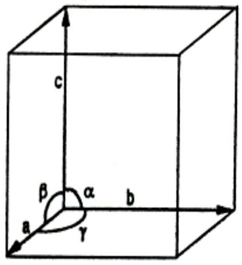


Figure 10: Diagram of a Crystal Unit Cell

A unit cell is said to be simple if it contains only one lattice point. A unit cell is said to be multiple if it contains several lattice points. The smallest unit cell that can describe the entire crystal is called the elementary unit cell.

2.3.6.1.1 Lattice Point

The points in the lattice where the particles are located are called lattice points. They can be derived from one another by translation with a vector: (u a + v b + w c), where (u, v, and w) are integers, and (a, b, c) are non-coplanar vectors chosen to have the smallest modulus.

2.3.6.1.2 The Motif or Structural Unit

The motif is the basic chemical entity that constitutes the crystal: it is the atom, molecule, or ionic group that occupies the lattice points of the crystal lattice.

2.3.6.2 The Crystal Systems

The description of a crystal is made using a system of three coordinate axes characterized by the lengths (a, b, c) of the direction vectors of the axes and by the angles (α, β, γ) that these axes form between them. These axes define the edges of the unit cell. The origin of the axes is taken at a lattice point. According to the symmetry of the crystal unit cell, there are seven basic crystal systems defined by:

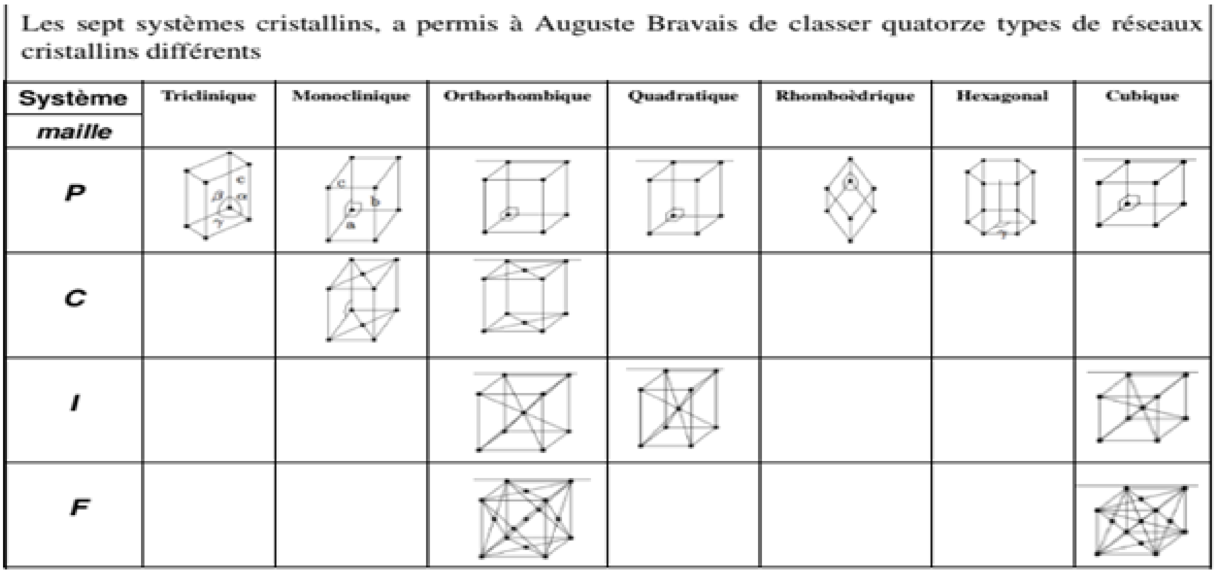
Tableau 2: The 7 Crystal Systems

Système	Longueurs des vecteurs directeurs des axes	Angles entre les axes
Cubique	a=b=c	α=β= γ=90°
Quadratique ou tétragonal	a=b≠c	α=β= γ=90°
Orthorhombique	a≠b≠c	α=β= γ=90°
Monoclinique	a≠b≠c	α= γ=90° β≠90°
Triclinique	a≠b≠c	α≠β≠γ≠90°
Hexagonal	a=b≠c	α=β= 90° γ=120°
Rhomboédrique	a=b=c	α=β= γ≠90°

2.3.6.3 The 14 Bravais Lattices

The seven crystal systems, as classified by Auguste Bravais, allow the classification of fourteen different types of crystal lattices.

Tableau 3: Les 14 Réseaux de BRAVAIS



Les sept systèmes cristallins, a permis à Auguste Bravais de classer quatorze types de réseaux cristallins différents

Système maille	Triclinique	Monoclinique	Orthorhombique	Quadratique	Rhomboèdrique	Hexagonal	Cubique
P							
C							
I							
F							

Several types of unit cells can correspond to the same crystal system. The cubic system, for example, gives rise to three lattices: simple cubic, body-centered cubic, and face-centered cubic. Depending on the lattice type, the 7 previous crystal systems give rise to the 14 Bravais lattices.

2.3.7 Characterization of a Crystalline Structure

An ideal crystalline structure is described by specifying the Bravais lattice, the motif or basis, and the atomic coordinates of each atom within the unit cell or a conventional cell.

2.3.7.1 Multiplicity (n)

The multiplicity nnn (or ZZZ) of a crystalline unit cell represents the number of motifs (or formula units) within that unit cell.

2.3.7.2 Compactness (C)

Compactness or packing density of a structure refers to the ratio of the volume actually occupied by atoms to the total volume of the unit cell:

$$\boxed{C = \frac{z\,4/3\,\pi\,r^3}{V_{maille}} \quad \text{avec} \quad V_{maille} = \vec{a}\,(\vec{b} \wedge \vec{c})}$$

The compactnessrate is also defined as**: τ=100C**

2.3.7.3 Coordination

In the hard-sphere model, the coordination number of a sphere is the number of neighboring spheres that are tangent to the considered sphere.

2.3.7.4 Density of a solid:

A mole corresponds to the quantity of matter in a system that contains as many elementary entities as there are atoms in 12 g of carbon-12. One mole of atoms contains 6.022×10^{23} atoms. This number is called Avogadro's number, after the Italian chemist who defined it.

$$\rho = \frac{\text{mass of solid in (g/cm3)}}{\text{its volume}}$$

$$\rho = \frac{z\,M_{motif}}{N\,v_{maille}}$$

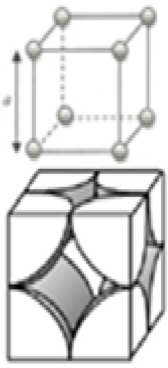
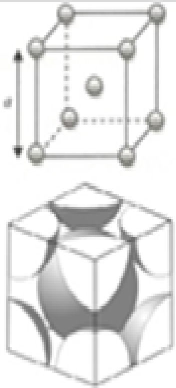
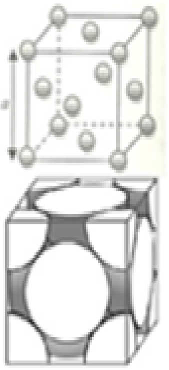
Where:

- Z = number of motifs per unit cell
- M_{motif} = molar mass of the motif
- N = Avogadro’s number
- V cell= volume of the unit cell

For solids: $\boldsymbol{\rho}$ (in g/cm3)=**d** (dimensionless)

$$d = \frac{\text{mass of certain solid without unit}}{\text{mass of the same volume of water}}$$

Tableau 4: Different crystallographic structures

	cubic	centered cubic	face-centered cubic
Cell			
Multiplicity	1	2	4
Condition of tengency	Tangent atoms on each edge 2R= a	Central atom tangent to vertex atoms 4R = a$\sqrt{3}$	Atom of a face tangent to the atoms at the vertices of the same face 4R = a$\sqrt{2}$
Compactness	51%	68%	74%
Coordination	6	8	12

The density **d** is an important data point in the study of crystalline structures, **d** is calculated from X-ray diffraction analysis results. It can also be measured experimentally. The comparison of these two values helps confirm the obtained structure.

2.3.7.5 Allotropy

A crystalline material can exist in one, two, or several forms corresponding to different arrangements of atoms, molecules, or ions within the unit cell. These different crystalline forms are called allotropes. An example of this is diamond and graphite, which are two allotropes of carbon. The phenomenon of allotropy corresponds to a change in crystal structure under the effect of temperature

2.3.7.6 Crystallographic Sites (Interstitial Sites)

Crystallographic sites correspond to interstitial voids between atoms. The most common ones are tetrahedral sites, defined by four atoms, and octahedral sites, defined by six atoms.

a) Tetrahedral sites:

A site is said to be tetrahedral if it is bounded by a tetrahedron formed by four neighboring atoms.

b) Octahedral sites:

A site is said to be octahedral if it is bounded by an octahedron formed by six neighboring atoms.

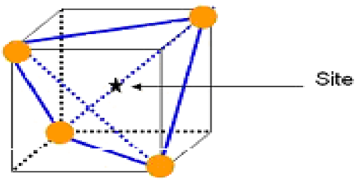


Figure 11 : Tetrahedral sites

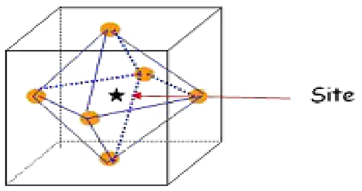


Figure 12 Octahedral sites

2.3.7.7 Crystallographic Lattice Row

A lattice row is any line passing through two lattice points. It is defined by the vector:

$$\vec{n} = u\vec{a} + v\vec{b} + w\vec{c}$$

where **u**, **v**, and **w** are coprime integers (integers with no common divisors). The notation for this lattice direction is **[u,v,w].** Every row corresponds to a family of identical parallel lattice rows passing through all the lattice points.

Note: Row [1,1,1] is pronounced as [one, one, one] Directions such as [100, [010],[001], Notice that the points [111], [222], [333], etc., define the same crystallographic or lattice direction.

A negative index is indicated by a bar over the number (e.g., $[1\bar{1}1]$

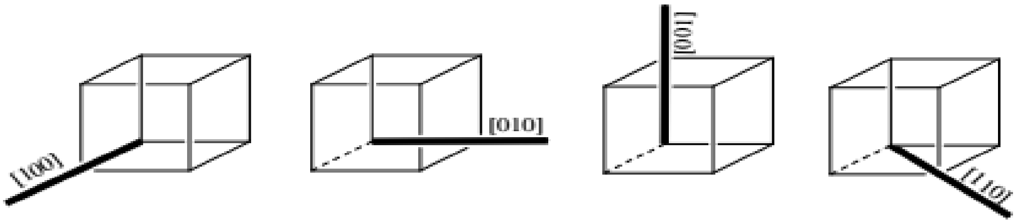


Figure 13 : different lattice rows

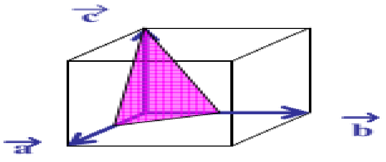
2.3.7.8 Crystallographic Lattice Planes

A lattice plane is a plane that passes through three non-collinear points (nodes) of the lattice.

The plane is designated by the indices \((hkl) \), called Miller indices, which can be positive, negative, or zero integers.

- A lattice plane is defined by three Miller indices \(h \), \(k \), and \(l \), such that:
  - ($h = a / x_0$)
  - ($k = b / y_0$)
  - ($l = c / z_0$)
  - a, b, and c are the lattice parameters.
- x0, y0, and z0 are the coordinates where the plane intersects the axes.
- The notation for the plane is ((hkl) .

- Consider the plane that intersects:
  - The x-axis at (a/2),
  - The y-axis at (b/2),
  - The z-axis at (c).



(2 2 1)

- The Miller indices of this plane are ((221).

2.3.8 Types of Interactions

2.3.8.1 Ionic Bonding: Insulators

A large difference in electronegativity (e.g., NaCl): the electropositive element tends to lose its valence electron (which is weakly bound); the electron is then gained by the electronegative element, leading to the formation of M^+ and X^-, in electrostatic equilibrium.

2.3.8.2 Covalent Bonding: Semiconductors

Very electronegative elements (e.g., diamond): valence electrons are shared through the formation of molecular orbitals.

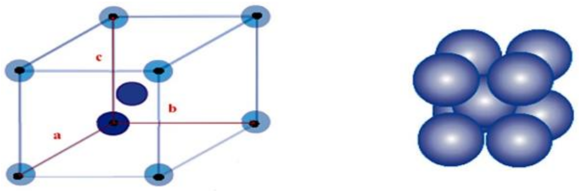
2.2.8.3- Metallic Bonding: Metals

Very electropositive elements (e.g., copper): valence electrons are loosely bound and free to move.

2.3.9 Metallic Crystals Structures

The atoms contained within a unit cell (to be specified in each case) form a crystal that results from the three-dimensional repetition of this motif following the translations of the associated lattice. Not all metallic crystals form structures with maximum compactness. Two lattices possess this property of maximum compactness: **the hexagonal close-packed lattice (hcp) and the face-centered cubic lattice (fcc).**

2.3.9.1 Body-Centered Cubic Structure (CC)



(a) (b)

Figure 14 : Centered Cubic Structure (CC)

2.3.9.2 face-centered cubic Structure (fcc).

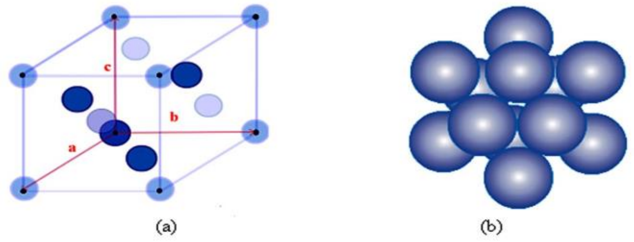


Figure 15 : Face-centered cubic lattice (FCC).

2.3.9.3 Compact hexagonal structure(HC)

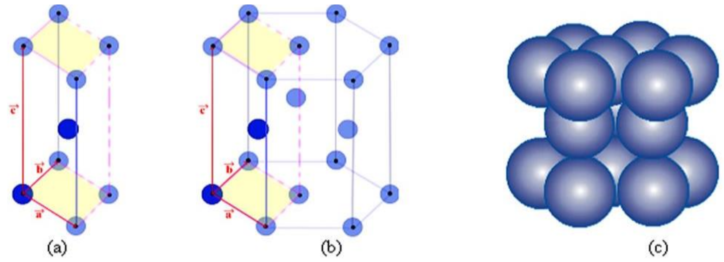


Figure 16 : Compact hexagonal structure (HC)

2.2.10- Ionic Crystals Structures

When the bonded atoms are different, the probability of the electron pair being near the more electronegative atom is higher (the electron cloud is asymmetric). When one of the two bonded atoms is highly electronegative (e.g., chlorine) and the other is highly electropositive (e.g., sodium), the electron pair remains primarily localized near the more electronegative atom (chlorine). In this case, the bond can be represented by a sodium atom that has lost an electron (**Na^+** ion) and a chlorine atom that has gained an electron (**Cl^-** ion). This is the model of the ionic bond.

This model has been experimentally confirmed through X-ray diffraction techniques for certain crystals. Electron density maps around the nuclei of the two bonded atoms have been established. Based on these maps, calculations have determined the total number of electrons around each atom. For NaCl, the results, within the limits of experimental error, show 10 electrons around Na and 18 around Cl. This corresponds well to the electron transfer:

$$Na \rightarrow Na^{+} + 1e^{-} \quad ; \quad Cl + 1e^{-} \rightarrow Cl^{-}$$

The interaction between the two ions formed is mainly due to the electrostatic attraction between two opposite charges. The ions formed often have the electron configuration of the nearest noble gas in the periodic table; they have 8 electrons in the outer shell (ns^2np^6).

This model, developed for the study of ionic bonding, is only an approximation. In most cases, the percentage of covalent bonding is not zero. However, it allows for the study of bond energy h good approximation by using simple electrostatic laws.

Stereochemistry of Some Cubic Structures of the MX Type

Since anions are larger than cations, they determine the type of packing, and the cations occupy the interstitial spaces within the anion lattice.

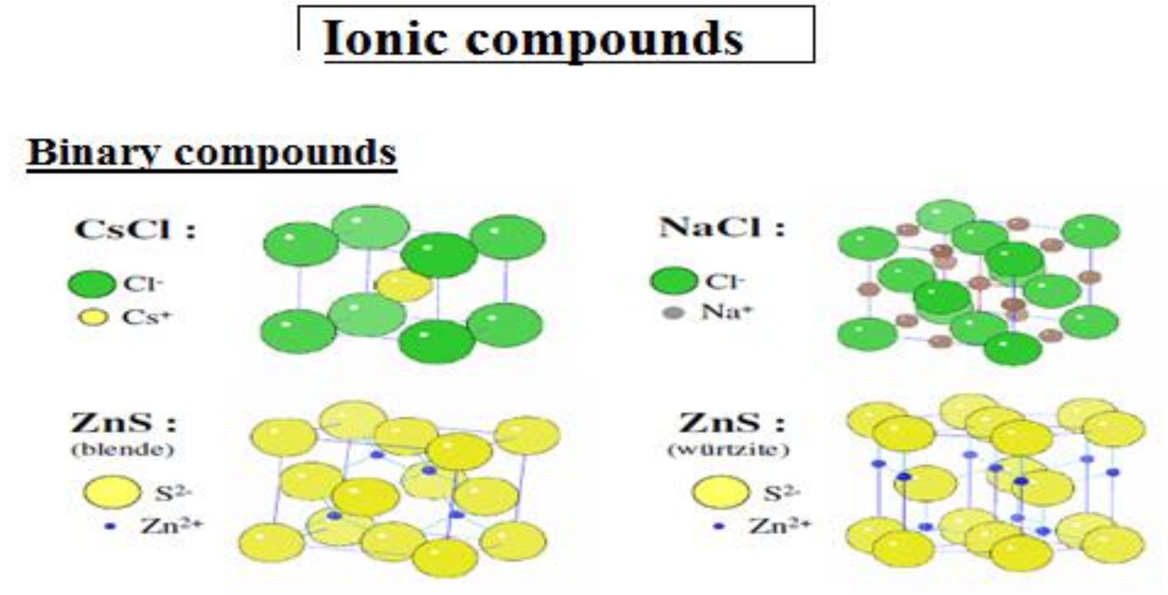


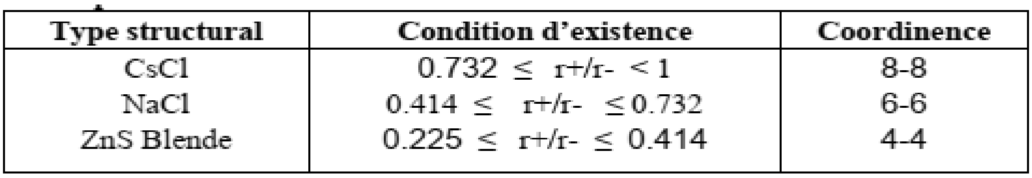
Figure 17 : MX type structures

Examples

Many compounds crystallize with the same structural type as ZnS (blende). Examples include: ZnO, ZnS, ZnSe, CdS, CuCl, CuBr, SiC, SnSi, GaP, InSb, and others.

Recap: Conditions for the stability of the three MX structures

Tableau 5Recap: Conditions for the stability of the three MX structures



Type structural	Condition d'existence	Coordinence
CsCl	$0.732 \leq r+/r- < 1$	8-8
NaCl	$0.414 \leq r+/r- \leq 0.732$	6-6
ZnS Blende	$0.225 \leq r+/r- \leq 0.414$	4-4

So the stability of ions in chemistry is determined by several factors, primarily focusing on the balance between attractive and repulsive forces. Electrostatic attraction between oppositely charged ions, as well as the size and charge of the ions themselves, play crucial roles. Additionally, the ease with which ions can form (influenced by ionization energy and electron affinity) and the arrangement of ions in a crystal lattice (for ionic compounds) are key consideration.

3 Chapter III Periodicity Of Elements

The atoms of chemical elements differ by their subatomic structure, which means the number and nature of the elementary particles that constitute them:

– **Nucleus:** Protons and, if present, neutrons;

– **Electron** cloud orbiting around the nucleus: Electrons, in a number equal to the protons in an atom at equilibrium.

Protons are positively charged (e^+), and electrons are negatively (**e**$^-$)charged, with equal elementary charges in absolute value, so that the atom is electrically neutral at equilibrium.

3.1 - Classification Of Chemical Elements

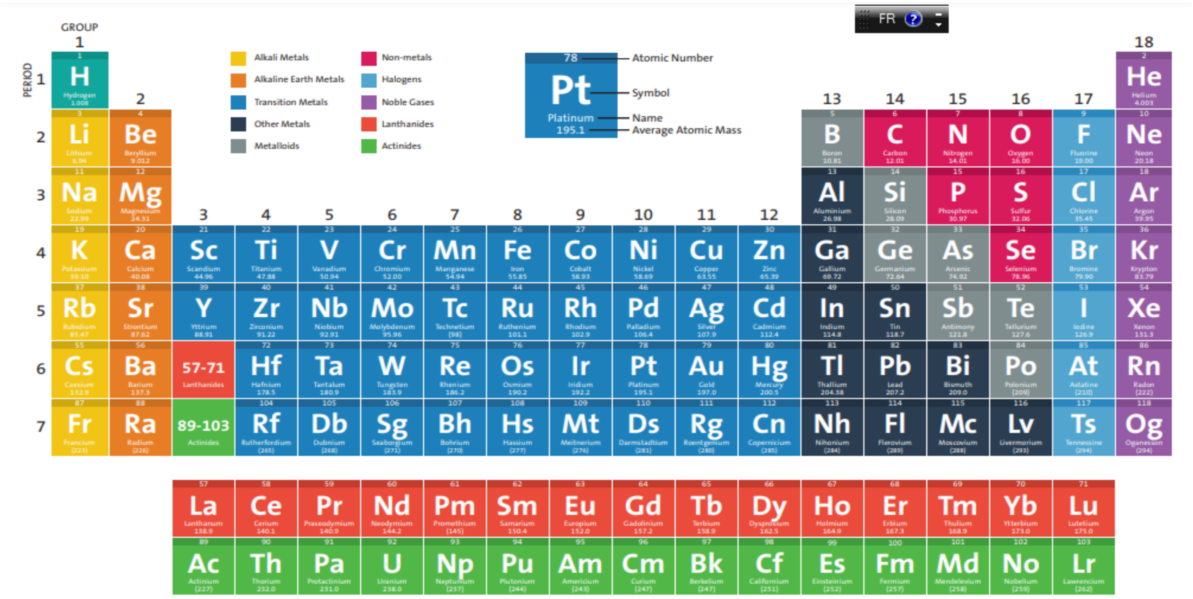


Figure 18 : MENDELEIEV TABLE

3.2 - Properties of Groups

The elements of Group VIII, called noble gases, are characterized by a complete outer electron shell, which gives them exceptional chemical stability.

The elements of Group IA (figur 20) have only one electron in their outer shells: they tend to lose it to achieve a full outer shell and form positive ions or cations. This tendency extends to all elements on the left side of the table, called metals, which are all electron donors.

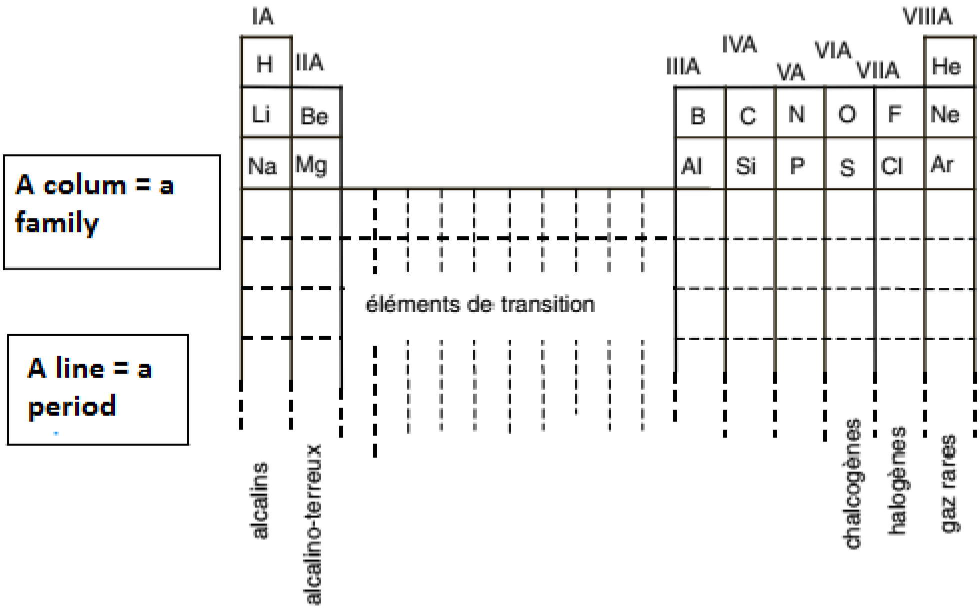


Figure 19 : The elements of Group

The elements of Group VIIA have seven electrons in their outer shells: they tend to complete the shell by capturing an available electron from their surroundings, forming negative ions or anions. This tendency also applies to certain elements on the right side of the table, called non-metals, which are all electron acceptors. Some elements located at the boundary between these two zones exhibit mixed properties, which vary depending on the electric field they are exposed to (they are semiconductors). Figure III.2 illustrates these behavioral differences through the band structures of these various types of atoms.

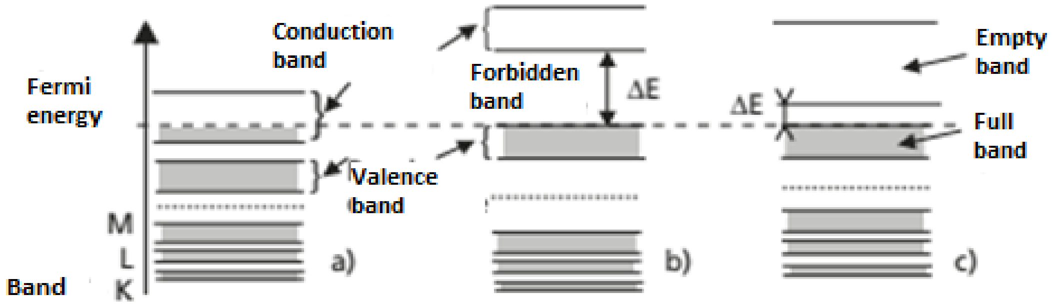


Figure 20 : Band structure diagrams

a) A cluster of metal atoms (the conduction band contains available states);

b) A cluster of non-metal atoms (the band gap has a large width ΔE\Delta EΔE);

c) A cluster of semiconductor atoms (the band gap has a small width).

3.3 - Recommended names for the groups of the periodic table:

1 - Alkali metals
2 - Alkaline earth metals
13 - Earth metals
14 - Carbonides
15 - Pnictogens (Nitrogen group)
16 - Chalcogens
17 - Halogens
18 - Noble gases / Inert gases

Groups 3 to 12 are transition elements (d1→10).

3.4 -Evolution and Periodicity of Elements Properties

3.4.1 Atomic radius (ra)

There are several definitions of the atomic radius. Its value can be obtained through experimental measurements or calculated from theoretical models.

The concept of the atomic radius is somewhat arbitrary. In fact, the radius can only be defined when the atom is part of a molecule, and it depends on the nature of the bonds.

- The atomic (or covalent) radius corresponds to half the distance between two atomic nuclei in a homonuclear diatomic molecule.

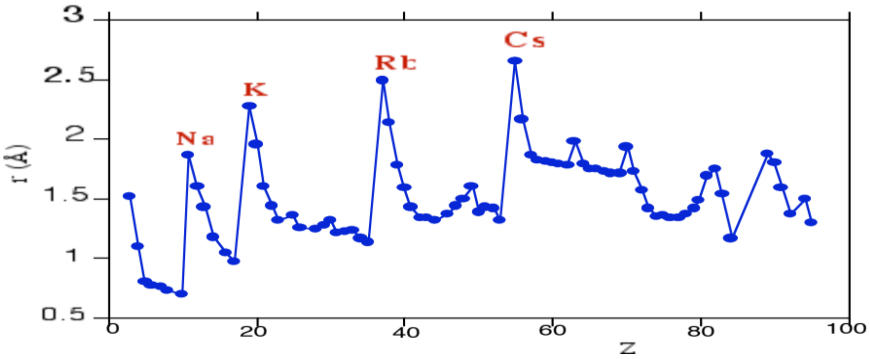


Figure 21 : Evolution Of Atomic Radius

- The radius of an atom corresponds to the average distance between the nucleus and the electron in the outer shell.

When moving from left to right across the same row (period) of the periodic table, electrons are added to the same shell. As the effective nuclear charge increases, the electrons experience greater attraction, causing the atoms to become more compact, and thus the atomic radius decreases.

In a period: if **Z** increases, then $\mathbf{r_a}$ decreases.

When moving down a group from top to bottom, the number of peripheral electrons increases because the number of shells increases, and consequently, the atomic radius increases.

In a group: if **Z** increases, then $\mathbf{r_{ar}}$ increases.

Z ↗ the n ↗ ⇒ volume, and thus the electron cloud increases and $\mathbf{r_{ar}}$↗

3.4.2 Ionization Energy (IE)

This is the energy that must be supplied (IE > 0) to an atom (or ion) to remove an electron from its ground state while in the gaseous state. This term only concerns the formation of cations.

In the same period, IE varies inversely with the atomic radius.

From top to bottom in the same group, the number of shells increases, and the valence electrons are increasingly distant from the nucleus. The nucleus/electron attraction weakens, making the outer electron easier to remove. The first ionization energy decreases from top to bottom within a group.

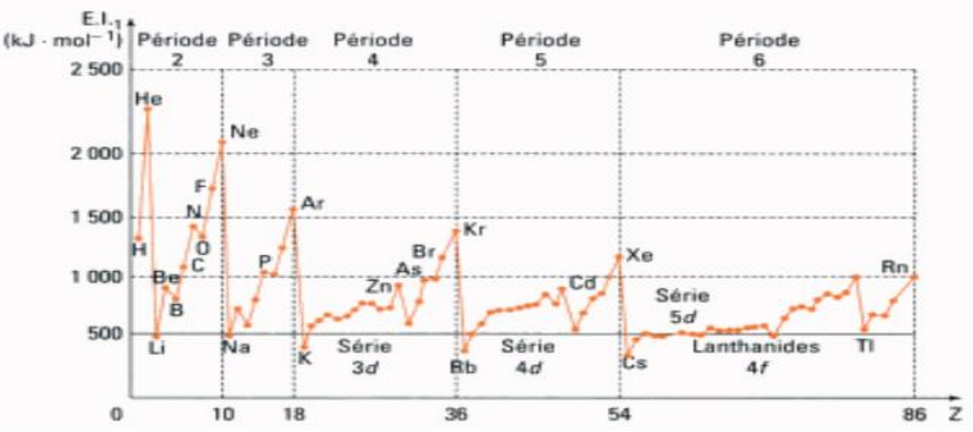


Figure 22 : Ionization Energy Evolution (IE)

3.4.3 Affinité électronique (A.E)

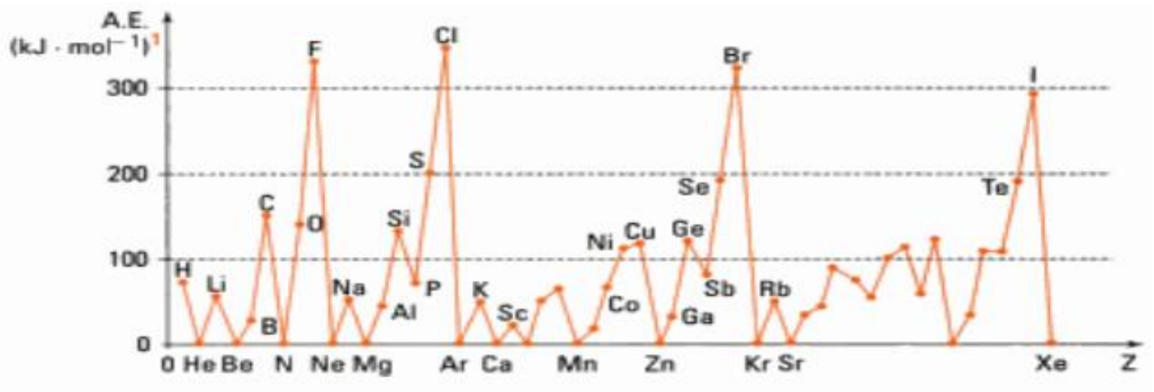


Figure 23 : Evolution of Electron Affinity

This is the opposite phenomenon of ionization. The electron affinity of an atom X is the energy released when this gas atom captures an electron.

$$A\,(g) + e^- \rightarrow A^-\,(g) + EA$$

In a period EA increases when Z increases

In a group EA decreases when Z increases

3.4.4 Electronegativity χ (E.N)

Electronegativity is the ability of an element to attract an electron. An element that easily loses one or more electrons is said to be electropositive.

- **The Mulliken scale of electronegativities**

Defines the electronegativity of an element X as the arithmetic mean of its ionization energy I.E(X) and its electron affinity E.A(X):

$$\chi_X^M = \frac{\mathbf{E.A(x) + I.E(X)}}{2}$$

Electronegativity is a dimensionless quantity that represents an element's ability to attract electrons in a bonding pair. An element that attracts electrons is said to be electronegative and has a high value of χ An electron donor element is electropositive, and the value of χ is low.

Electronegativity varies in the same direction as ionization energy, meaning:

- From left to right across a period, Z increases, and E.N increases.
- From top to bottom within a group, Z increases, and E.N decreases.

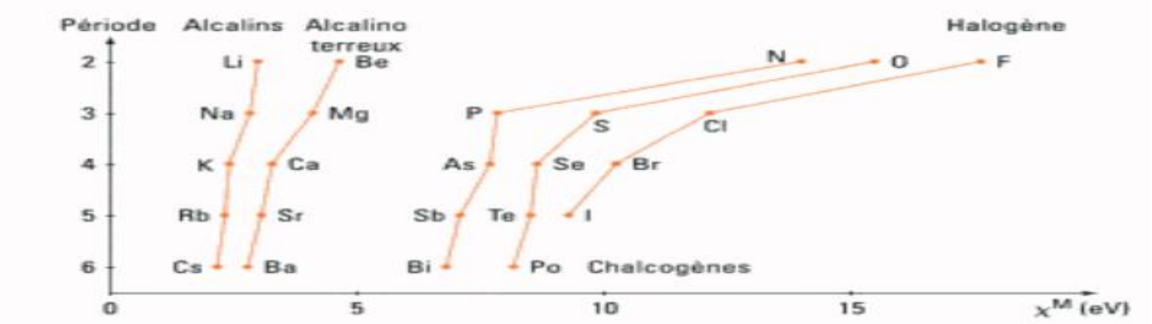


Figure 24 : Evolution of Electronegativity

➢ Pauling Electronegativity:

Consider the bond between two atoms, A and B. Each atom can also form other bonds. If the atoms have the same electronegativity, they will have an equal tendency to attract the bonding electron pair, and the pair will be, on average, halfway between the two atoms. To achieve this type of bond, A and B must be atoms of the same element.
The difference in electronegativity between atoms A and B is calculated as follows:

$$x_A - x_B = (eV)^{\frac{1}{2}}\sqrt{E_{d(AB)} - \frac{\sqrt{(E_{d(AA)} + E_{d(BB)})}}{2}}$$

Where:

- $Ed_{(AB)}$ is the dissociation energy of the A-B bond, expressed in electronvolts (eV).
- The factor (eV$^{)-1/2}$ is included to ensure a dimensionless result.

The union of two atoms with the same electronegativity will result in a pure covalent bond.

- A slight difference in electronegativity will create a polar covalent bond.
- A large difference in electronegativity will result in an ionic bond.
- A $\Delta\chi \leq 1.2$ will give a covalent bond.
- A $\Delta\chi \approx 1.5$ will give a moderately ionic bond.
- A $\Delta\chi \geq 2.0$ will give an ionic bond.

3.5 Characteristics of Metals and Non-Metals

3.5.1 Common properties of metals

- They have a shiny and lustrous appearance.
- They conduct electricity and heat.
- They are malleable enough to take on different shapes.
- They are ductile, meaning they can be stretched into thin wires.
- They have high density; lead is the densest of all metals.
- Most metals have high melting points, which means they are solid at room temperature.
- Mercury is the only metal that is liquid at room temperature.
- Cesium and gallium have low melting points (below 30ºC).
- Metals do not chemically combine with each other but react with non-metals to form compounds.
- Among metals, alkali metals (Group 1) are the most reactive.
- Metals near the center of the periodic table are the least reactive.
- The least reactive metals, such as copper, silver, and gold, are the most likely to be found in a pure state in nature.
- The most reactive metals, such as lithium and sodium, are never found in a pure state in nature.

The tendency of metal atoms to easily lose their valence electrons explains many of their properties, such as their large atomic radii, low ionization energies, and low electronegativities. This is why they can be shaped without breaking. Metals are both malleable and ductile, meaning they can also be stretched into thin wires. The ability of their valence electrons to move relatively freely makes them good conductors of heat and electricity.

3.5.2 Chemical Properties

Metals differ chemically from non-metals in that they form positive ions, basic oxides, and hydroxides. When exposed to moist air, many metals corrode, meaning they undergo chemical reactions. For example, iron rusts because the oxygen in the atmosphere reacts with the metal to form its oxide.

Aluminum and zinc appear unaffected by this process, but they are actually covered almost instantly by a thin layer of oxide, preventing further chemical reaction in the metal. Tin, lead, and copper react slowly under normal conditions. Silver reacts with compounds such as sulfur dioxide and tarnishes when exposed to air containing these compounds. Metals combine with non-metals to form salts.

4 Chapter IV Major Mineral Syntheses

Inorganic chemistry deals with the synthesis, structure, and properties of solid materials. It once involved how to produce iron and copper through processes that connected solid-state chemistry to the origins of civilizations. These ancient civilizations knew how to synthesize/extract metals and create new pigments via simple reactions carried out in a specific order, either through the power of fire or in solution, using techniques such as grinding and filtration. Inorganic synthesis, governed by scientific laws and relying on various techniques, quickly allows for the discovery of many materials with sought-after properties, driving the development of the technologies of today and tomorrow.

4.1 Halogens (Group 17)

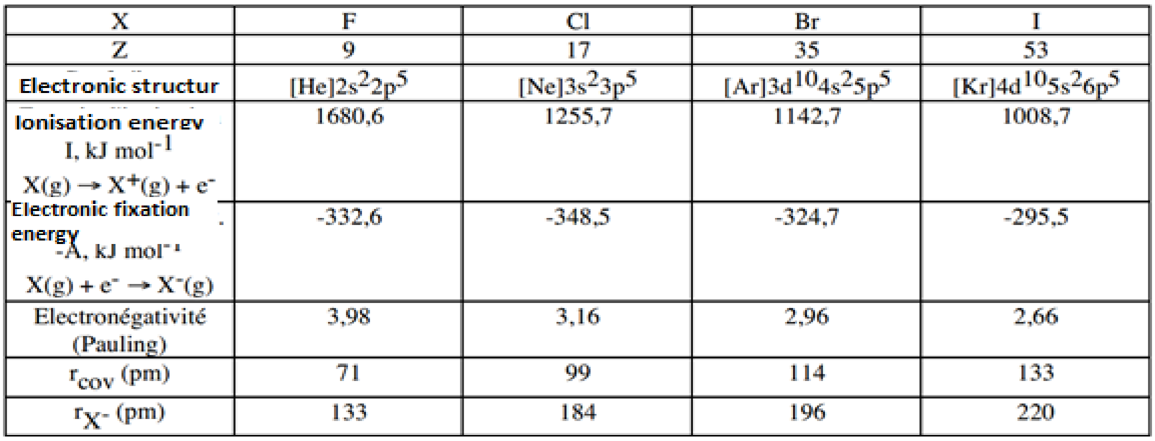
The elements in column 17 are called halogens and are characterized by a fundamental electronic configuration of **$(ns)^2(np)^5$**, meaning they have 7 valence electrons. The elements in the group are:

- n = 2 : Fluorine F, [He] $(2s)^2(2p)^5$;
- n = 3 : Chlorine Cl, [Ne] $(3s)^2(3p)^5$;
- n = 4 : Bromine Br, [Ar] $(4s)^2(3d)10(4p)^5$;
- n = 5 : Iodine I, [Kr] $(5s)^2(4d)^{10}(5p)^5$.
- n = 6 Astatine, At,[Xe] $(6s)^2(5d)^{10}(4f)^{14}(6p)^5$; is radioactive, as its name suggests (which means "unstable").

4.1.1 Atomic Properties

The atomic properties of the halogens, presented in the table below, are discussed in more detail graphically afterward.

Tableau 6The atomic properties of the halogens

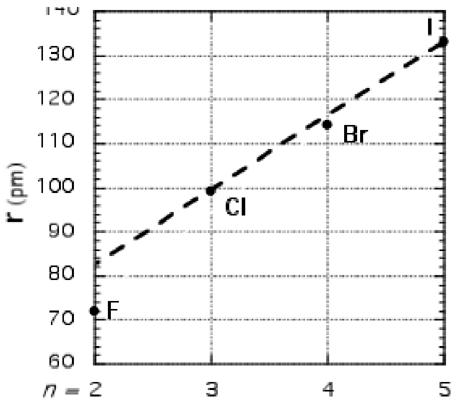


X	F	Cl	Br	I
Z	9	17	35	53
Electronic structur	[He]$2s^22p^5$	[Ne]$3s^23p^5$	[Ar]$3d^{10}4s^25p^5$	[Kr]$4d^{10}5s^26p^5$
Ionisation energy I, kJ mol^{-1} $X(g) \rightarrow X^+(g) + e^-$	1680,6	1255,7	1142,7	1008,7
Electronic fixation energy -A, kJ mol^{-1} $X(g) + e^- \rightarrow X^-(g)$	-332,6	-348,5	-324,7	-295,5
Electronégativité (Pauling)	3,98	3,16	2,96	2,66
r_{cov} (pm)	71	99	114	133
r_{X^-} (pm)	133	184	196	220

4.1.1.1 Atomic radius

As expected, the atomic radius increases as we move down the column.

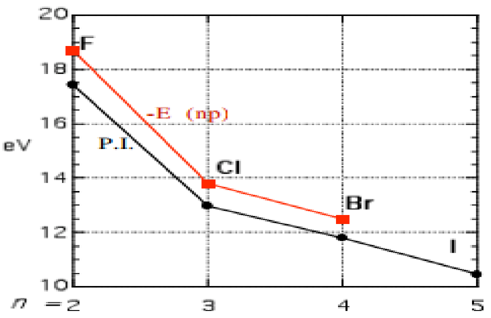
Fluorine, however, is particularly small. Fluorine electrons are constrained to a small region of space, and the effects of interelectronic repulsion will be particularly strong.

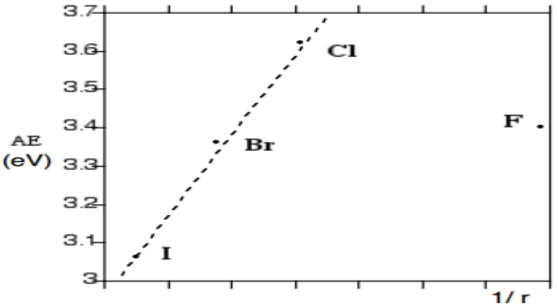


4.1.1.2 Ionization Potential

To ionize a halogen element, an electron must be removed from the (np) level into the vacuum. Since the effective nuclear charge Z* is high in group 17, these (np) orbitals are deeply bound, and the corresponding ionization potential is high.

Again, this effect is particularly pronounced for fluorine.





4.1.1.3 Oxidation States and Electron Affinities:

Fluorine is assigned an oxidation number of -1 in all its compounds because it is the most electronegative of all elements. Other halogens exhibit a wide range of oxidation numbers, and the redox chemistry of these halogens is significant.

The oxidation number is generally odd; compounds with even oxidation numbers are often thermally unstable. Chlorine is the third most electronegative element after fluorine and oxygen. Halide ions readily form by accepting an electron, completing their valence electron octet. The electron affinity decreases as we move down the group.

4.1.2 Summary of Common Properties:

- Very high electronegativities
- Seven valence electrons (one less than a stable octet)
- Very high reactivity, particularly with alkali metals and alkaline earth metals

4.1.2.1 Chemical Properties

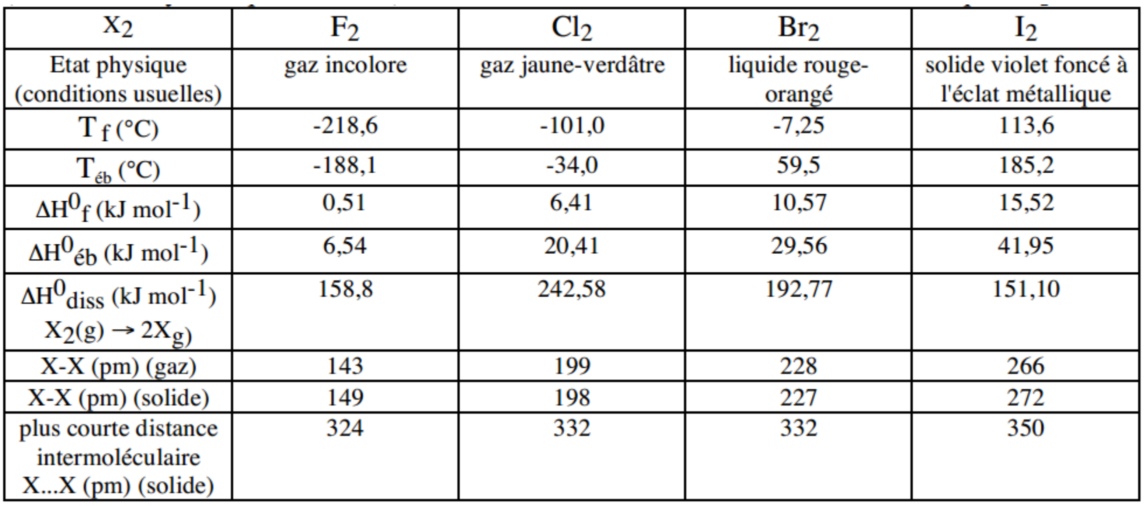
- All halogens have seven valence electrons, forming ions with a -1 charge.
- Fluorine is the most reactive of all elements and is difficult to handle.
- Iodine sublimes when heated.

4.1.3 Dihalogen Molecules

Halogens can combine with each other to form interhalogen ions and polyhalide ions. Polyhalide ions have the basic formula **[Y–X–Y]⁻**, where X cannot be fluorine because it cannot expand its octet.

The halogen elements, in their most stable state at **298 K** under 1 bar pressure (standard thermodynamic state), exist as diatomic molecules **X_2**.

Tableau 7: Dihalogen Molecules



X_2	F_2	Cl_2	Br_2	I_2
Etat physique (conditions usuelles)	gaz incolore	gaz jaune-verdâtre	liquide rouge-orangé	solide violet foncé à l'éclat métallique
T_f (°C)	-218,6	-101,0	-7,25	113,6
$T_{éb}$ (°C)	-188,1	-34,0	59,5	185,2
ΔH^0_f (kJ mol^{-1})	0,51	6,41	10,57	15,52
$\Delta H^0_{éb}$ (kJ mol^{-1})	6,54	20,41	29,56	41,95
ΔH^0_{diss} (kJ mol^{-1}) $X_2(g) \rightarrow 2X_{g)}$	158,8	242,58	192,77	151,10
X-X (pm) (gaz)	143	199	228	266
X-X (pm) (solide)	149	198	227	272
plus courte distance intermoléculaire X...X (pm) (solide)	324	332	332	350

4.1.3.1 Metallic Halides

Halogens form a set of non-metals that are very similar. They exist as diatomic molecules, X2X_2X2, which oxidize metals to form halides (with energy release).

Example:

$$X_2 + M \rightarrow MX_2$$
$$Cu + Cl_2 \rightarrow CuCl_2$$

- **Oxidizing Power:**

The chemical activity decreases from fluorine to iodine:

1. Fluorine displaces chlorine, bromine, and iodine.
2. Chlorine displaces bromine and iodine.
3. Bromine displaces iodine.

$$Cl_2 + 2NaBr \rightarrow Br_2 + 2NaCl$$
$$Cl_2 + 2KI \rightarrow I_2 + 2KCl$$
$$Br2 + 2KI \rightarrow I_2 + 2KBr$$

- **Reaction with Non-Metals**

$$2P + 3\,Cl2 \rightarrow 2PCl3 \quad (P\ III)$$
$$PCl3 + Cl2 \rightarrow PCl5 \quad (PV)$$

1.The oxides of halogens are acidic.

2. Their hydrogen compounds are covalent.

Fluorine is the most electronegative element in the periodic table. Generally, electronegativity and oxidizing power decrease as you go down the group. This increases the covalent character of the compounds, such that AlF_3 is ionic while $AlCl_3$ is covalent.

Note:

- The main chemical characteristic of halogens is their oxidizing power.
- Fluorine shows some anomalies due to its small atomic and ionic size. The F-F bond is weaker than expected because the small size of the F atom brings lone pairs closer together than in other halogens, leading to increased repulsion and bond weakening.
- Fluorine has the highest oxidizing power, so elements combining with fluorine have the highest oxidation states. Fluorine is such a strong oxidizing agent that it must be

prepared by electrolysis.

Chlorine is the next strongest oxidizing agent after fluorine, but it is prepared by chemical oxidation.

4.1.3.2 Hydrogen Halides

Hydrogen halides have the basic formula HXHXHX.
HF is a colorless liquid that boils at 19.5°C. All other hydrogen halides are odorless gases. HF is a liquid due to hydrogen bonds between the molecules. All hydrogen halides dissolve easily to form acidic solutions, with the most commonly used being hydrochloric acid (HCl).

$$H_2 + X_2 \rightarrow 2HX$$

All, except HF, are typical acids. HF is a weak acid because the H-F bond is strong and hydrogen bonding occurs between (F^-) and HF in solution. HCl, HBr, and HI are strong Brønsted acids in aqueous solution. This means that the deprotonation reactions:

$$HXaq = H^+aq + X^-aq$$

are favored. In other words, their ΔrG is negative, or the pKa of these acids is negative

$$(\mathbf{pKa} = \frac{\Delta \mathbf{rG°}}{\mathbf{2{,}3RT}}).$$

Table 1 PKa and ΔrG of Halid

Acide	$\Delta_rG°$ (kJ/mol)	pKa
HF	+ 18,1	3,2
HCl	- 39,7	-7
HBr	- 54,0	-9,5
HI	- 57,3	-10

4.1.3.3 Halogen/Oxygen Compounds

Fluorine/Oxygen Compounds

Fluorine must be distinguished from other halogens. As previously noted, fluorine is more electronegative than oxygen. The only fluorine oxoacid, HOF, is unstable at room temperature.

Example 1:
Fluorine with silicon oxide (glass): : $\mathbf{2F_2 + SiO_2 \rightarrow SiF_4 + O_2}$

Example 2: $\mathbf{2F_2 + 2H_2O \rightarrow 4HF + O_2}$

4.1.3.4 Compounds of Other Halogens

Variability of Oxidation States: Oxides and Oxoacids.

Chlorine, bromine, and iodine, which are less electronegative than oxygen, form true oxides. Since they can exceed the octet, compounds with various oxidation states are observed. Their reactions with water yield oxoacids, resulting in rich chemistry. Many oxides are metastable (their free enthalpy of formation is positive; since their enthalpy of formation is also positive, they are called "endothermic") and decompose violently when activated. Since halogens have 7 valence electrons, all oxidation states from +I to +VII must be considered.

Chlorine, bromine, and iodine form several thermally unstable oxides, such as chlorine dioxide **ClO_2.** The most well-known salts are hypochlorite, chlorate (I) **ClO^-**, chlorite, chlorate (III) **ClO_2**, chlorate (V) **ClO_3^-** , and perchlorate (VII) **ClO_4^-**. All these salts are powerful oxidizing agents.

Example: $2F_2 + 2H_2O \rightarrow 4HF + O_2$

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$
$$Br_2 + H_2O \rightarrow HBr + HOBr$$

4.1.4 Halogens and Electrochemical Synthesis

Halogens are very reactive and are not found in their free state. However, except for astatine (which is radioactive and short-lived), they are found in combined forms in the Earth's crust. Fluorine is the 13th most abundant element by weight in the Earth's crust, while chlorine is the 20th. Bromine and iodine are relatively rare. The main source of fluorine is fluorite (**CaF_2**) or fluoroapatite. The name "fluorite" comes from the fluorescence of the mineral, meaning it emits light when heated.

Interestingly, seawater contains small amounts of fluorine, though large amounts of **Ca^{2+}** in the sea contribute to the formation of insoluble **CaF_2**. The most abundant chlorine compound is **NaCl**, used to produce nearly all **Cl_2** and **HCl**.

Bromine is found in seawater, and iodine is normally concentrated in algae.

Halogen compounds are generally ionic, and their separation requires an electrolytic process.

Electrolytes :

An electrolytic cell involves two electrodes immersed in an electrolyte solution and connected to a power source. When an electric voltage is applied, an electric field is created between the electrodes, directing the movement of ions in the solution as follows: positive ions move toward the negative electrode, and negative ions move toward the positive electrode. This process is called electrolysis. The electrode connected to the negative pole of the power source becomes the negative pole (called the cathode), and the electrode connected to the positive pole becomes the positive pole of the cell (called the anode). Positively charged ions, attracted to the cathode, are called cations, while negatively charged ions, moving toward the anode, are called anions.

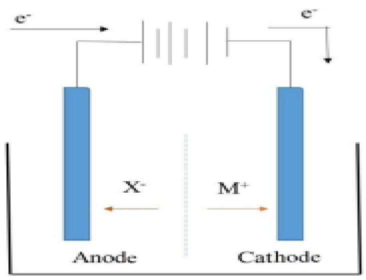


Figure 25: Electrolyte cell

Cathode (negative pole) : $M^+ + e^- \rightarrow M$ **(réduction)**

Anode (positive pole) : $X^- \rightarrow X + e-$ **(oxydation)**

4.1.4.1 Fluorine

Fluorine is very reactive, making its production and handling difficult. It is obtained by treating **CaF_2** with **H_2SO_4** to form an aqueous mixture of **HF**. It is then distilled to give anhydrous **HF** liquid. A cooled solution of **KHF_2** in the presence of anhydrous **HF** is then electrolyzed to produce **F_2** and **H_2**.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

$$KF + HF \rightarrow K[HF_2]$$

$$HF + K[HF_2] \rightarrow H_2 + F_2 \quad \text{(under electrolysis)}$$

That said, the production of fluorine presents many difficulties; HF is toxic and has a corrosive effect on glass and tissues. Fluorine is very reactive, it attacks glass and ignites in the presence of traces of gallium and crystalline silicon.

4.1.4.2 Chlorine

The name chlorine is derived from the Greek word "chloros," meaning pale green. It is a dense, yellow-green gas with a choking odor. Chlorine is very toxic and was used as a weapon during World War I. It is produced on a large scale by the electrolysis of aqueous or anhydrous NaCl (sodium chloride) during the production of NaOH and sodium metal.

Particles present in the electrolyte:

$$\mathbf{Na^{+}_{(aq)}\quad Cl^{-}_{(aq)}\quad H^{+}_{(aq)}\quad OH^{-}_{(aq)}}$$

$$\mathbf{H_2O_{(l)} \rightarrow H^{+}_{(aq)} + OH^{-}_{(aq)}}$$

Protons and hydroxyl ions are continuously present because, at any moment, 1 in 10 million water molecules dissociates into ions. Although the proportion of hydrogen is small, the number of protons and hydroxyl ions is significant.

At the cathode (-):

Both Na+ and H+ are attracted, but since sodium is above hydrogen in the reactivity series, it is easier to give electrons to **H+** than to **Na+** is not discharged.

$$\mathbf{2H^{+}(aq) + 2e^{-} \rightarrow H_2\ (aq)}$$

As hydrogen ions are constantly removed from the water, the concentration of OH−\text{OH}^-OH− increases around the cathode, meaning the solution becomes increasingly alkaline, as indicated by pH paper turning blue-purple. Sodium ions are also present in the solution near the cathode. The strong alkaline sodium hydroxide can then be extracted from the solution.

At the anode (+):

$$\mathbf{2Cl^{-}_{(aq)} - 2e- \rightarrow Cl_2}$$

Chloride ions are attracted and discharged.

Note: Since chlorine reacts with sodium hydroxide, a method must be found to keep the sodium hydroxide produced at the anode separate. One industrial technique is to keep the electrolyte higher than the anode to minimize the diffusion of hydroxide ions across the diaphragm between the electrodes. The cell used in industry is called a "diaphragm cell."

As for the other elements in the group, bromine is obtained by treating brine from pools or seawater. Iodine is obtained from brine as well as from algae like kelp. Astatine is radioactive, and there is estimated to be less than 30 grams of it in the Earth's crust. To obtain it in quantity, it must be synthesized in the laboratory.

The reactivity of chlorides decreases from top to bottom:

$$Cl_2 + 2NaBr \rightarrow Br_2 + 2NaCl$$

$$Cl_2 + 2KI \rightarrow I_2 + 2KCl$$

$$Br_2 + 2KI \rightarrow I_2 + 2KBr$$

4.2 Chalcogens (Group 16)

These elements are characterized by a fundamental electronic configuration of $(ns)^{2(}np)^{4}$, meaning they have 6 valence electrons.

1. **Oxygen « $_8$O »**: ([He] $(2s)^2(2p)^4$
2. **Sulfur « $_{16}$S »**: ([Ne] $(3s)^2(3p)^4$
3. **Selenium « $_{34}$Se »**: (Se, [Ar] $(4s)^2(4p)^4$
4. **Tellurium « $_{52}$Te »**: [Kr] $(5s)^2(5p)^4$.
5. **Le polonium « $_{84}$ Po »**: ([Xe] $(6s)^2(5d)^{10}(4f)^{14}(6p^{)4})$, a radioactive metal.

Atomic Properties:

Evolution of atomic radius, ionization energy, and electron affinity.

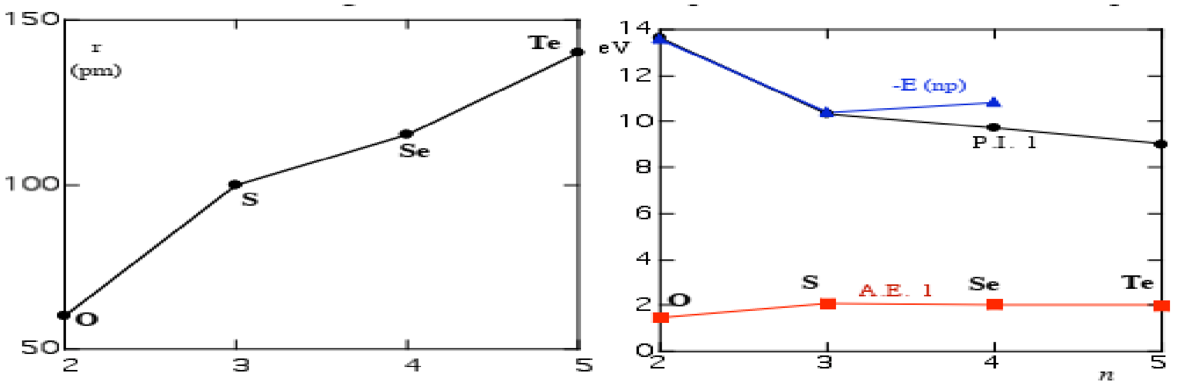


Figure 26 : Evolution of atomic Properties:

4.2.1 Dioxygen (O_2)

Dioxygen is a colorless, odorless, and tasteless gas under normal temperature and pressure conditions. It participates in redox reactions, primarily combustion, corrosion, and respiration. Dioxygen is one of the allotropic forms of oxygen.

4.2.1.1 Industrial Production of (O_2)

Dioxygen is produced industrially, primarily (95%), by cryogenic separation of air components, i.e., by liquefaction of air followed by fractional distillation. The critical temperatures of nitrogen **N_2**, **(tc=−146.9°C)** and dioxygen **O_2 (tc=−118.4°C)** do not allow air to be liquefied by simple compression. Therefore, the air must be compressed between 5 and 7 bar, filtered, dried, decarbonated by adsorption on molecular sieves, and finally cooled by heat exchange between the incoming gas and the liquefied gases. The refrigeration losses are compensated by expansion of 5-10% of the treated gas flow in a turbine, whose external work is recoverable. The distillation, in the most commonly used process, is carried out...

4.2.1.2 Laboratory Production

Dioxygen can be prepared by electrolysis of water, but this technique is slow and energy-consuming. A quick way to release a large quantity of dioxygen is to dissolve oxylith tablets (**Na_2O_2**). Today, liquid dioxygen is used for medical and industrial applications. O_2 can also be prepared from oxygen-rich substances such as:

1. The decomposition of **H_2O_2** (catalyzed by MnO_2:

$$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$$

2. The decomposition of hypochlorite (catalyzed by light and **Co^{2+}**):

$$2NaClO \rightarrow 2NaCl + O_2\uparrow$$

3. The thermal decomposition of transition metal oxides:

$$2HgO \rightarrow 2Hg + O_2\uparrow$$
$$2PbO_2 \rightarrow 2PbO + O_2\uparrow$$

4. The thermal decomposition of **$KMnO_4$**:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

4.2.2 Sulfur (S)

Sulfur is a chemical element of the chalcogen family, symbol S, with atomic number 16. It is a multivalent non-metal, abundant, tasteless, and insoluble in water. Sulfur exists in solid, liquid, and gaseous forms. The ordinary solid forms of sulfur at room temperature are based on various crystalline arrangements of cyclo-S_8, forming a "crown-shaped ring."

Sulfur is found in nature in large quantities, attached to other elements in the form of sulfides (e.g., pyrite, cinnabar, galena, sphalerite, and stibnite) and sulfates (e.g., gypsum, barite, vitriols). It is also found in free form at hot springs, fumaroles, and more generally in volcanic gases. In its free form, sulfur is also present in ores. Sulfur is one of the most used radionuclides in biological and medical research.

$$FeS_2 + 2HCl \rightarrow FeCl_2 + H_2S$$

$$2FeS_2 + (11/2)O_2 \rightarrow Fe_2O_3 + 4SO_2$$

4.2.2.1 Sulffuric Acid Snthesis

Sulfuric acid is obtained from native sulfur, hydrogen sulfides, or generally from ores such as cinnabar, galena, sphalerite, stibnite, and pyrite rocks. The two processes for synthesizing sulfuric acid both begin with the production of a mixture of air and sulfur dioxide **(SO_2)**, either by burning sulfur or hydrogen sulfide (a byproduct of a neighboring industry), roasting a sulfide (e.g., cinnabar, galena, sphalerite), or decomposing a sulfate like anhydrite.

First Step:

Production of Sulfur Dioxide (SO_2):

Roasting of sulfide ores

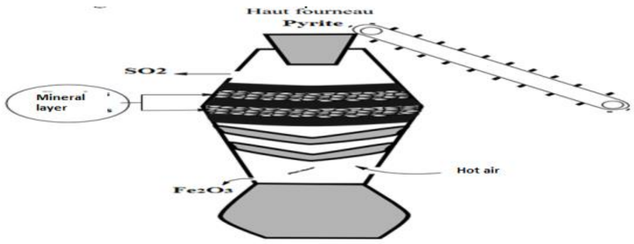


Figure 27 : Roasting of sulfide ores

Example:

- Pyrite **(FeS_2)**: $2FeS_2 + (11/2)O_2 \rightarrow Fe_2O_3 + 4SO_2$

If the pyrite mass is large enough, the heat generated by the double oxidation is sufficient to sustain the reaction. Pyrite is self-combustible.

- **Combustion of sulfur:**
  Large quantities of sulfur are converted to sulfur dioxide by simple combustion in air. This process is more expensive than roasting natural sulfides.

$$S + O_2 \rightarrow SO_2$$

Second Step:

The second step can generally be produced using two processes. The first is known as the lead chamber process and the second as the contact process.

1. Lead Chamber Process:

The principle is the oxidation of sulfur dioxide gas by air in the presence of water, catalyzed by nitrogen oxides.

$$SO_2\,(gaz) \;+\; \tfrac{1}{2}\,O_2 + \;H_2O\,(vapeur) \xrightarrow{NO,\;NO_2} H_2SO_4$$

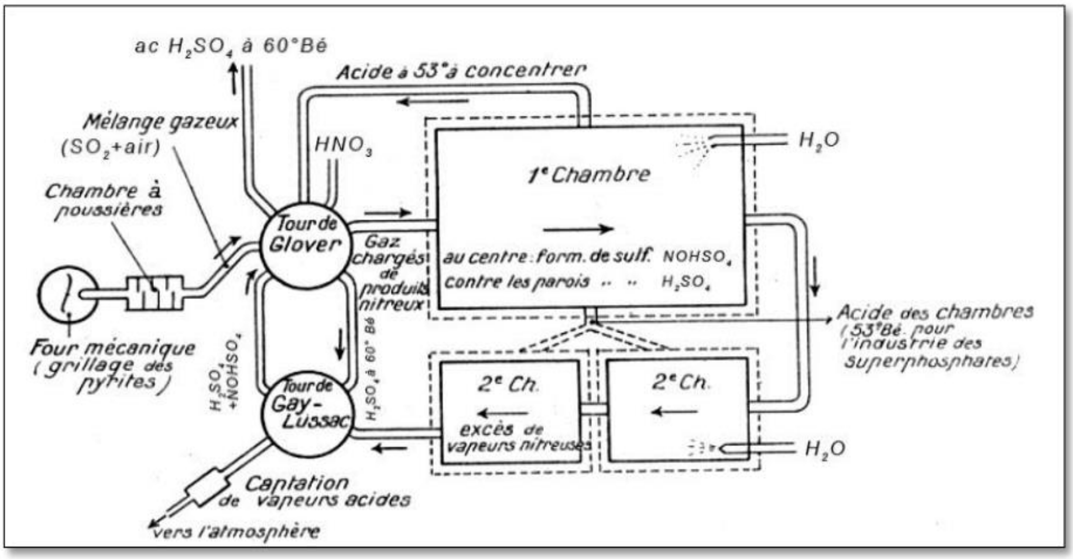


Figure 28 : Diagram of the Installation for the Lead Chamber Process

2. Contact Process

The most widely implemented industrial process today, called the "Contact Process," is broken down into three steps:

1. Preparation and Purification of Sulfur Dioxide (SO_2):

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g)$$

2. Oxidation of Sulfur Dioxide to Sulfur Trioxide or Sulfuric Anhydride (SO_3) using Vanadium Pentoxide (V_2O_5):

$$2SO_2\,(g) \; + \; O_2(g) \rightarrow 2SO_3\,(g) \qquad \Delta H = -197 Kj/mol$$

The sulfur trioxide is then cooled in a heat exchanger and collected in an absorption tower, where it is dissolved in concentrated sulfuric acid to produce oleum:

$$SO_3 \; + \; H_2SO_4\,(l) \rightarrow H_2S_2O_7\,(l)$$

Oleum is then hydrated to release sulfuric acid:

$$H_2S_2O_7\,(l) \; + \; H_2O\,(l) \rightarrow 2H_2SO_4\,(l)$$

The so-called "double catalysis" or "inter-absorption" process is used to improve the conversion rate, achieving rates as high as 99.8%.

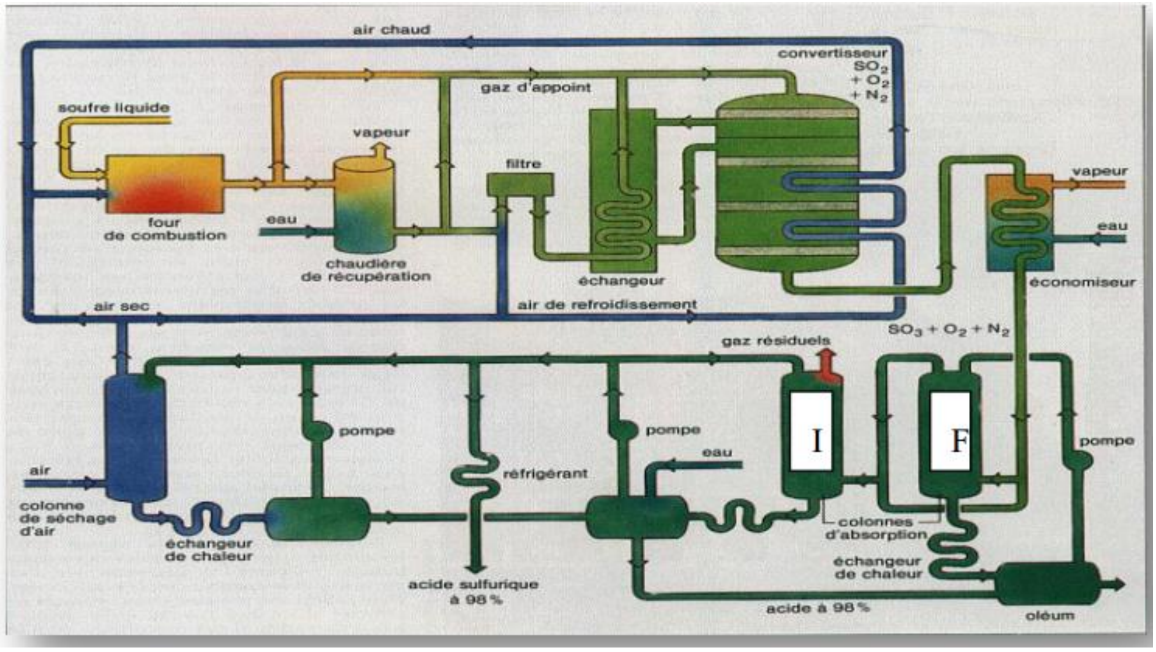


Figure 29 : Diagram of Sulfuric Acid Preparation by the Contact Process

4.3 Pnictogen (Group 15)

These elements are characterized by a fundamental electronic configuration: (ns)2(np)3, meaning they have 5 valence electrons. **The Group VA elements are:**

1. **Nitrogen (N)** (non-metal) **« $_7$N »**: ([He] $(2s)^2(2p)^3$
2. **Phosphorus (P)** (non-metal) **) « $_{15}$P »:** ([Ne] $(3s)^2(3p)^3$

3. **Arsenic (As)** (semi-metal) **« $_{33}$As »:** ([Ar] $(4s)^2(4p)^3$

4. **Antimony (Sb)** (semi-metal) **« $_{51}$Sb »:** ([Kr] $(5s)^2(5p)^3$).
5. **Bismuth (Bi)** (metal) **« $_{83}$ Bi »:** ([Xe] $(6s)^2(5d)^{10}(4f)^{14}$ $(6p)^3$) , a radioactive metal.

4.3.1 Nitrogen

Elemental nitrogen exists as dinitrogen. The fundamental electronic configuration of dinitrogen is **$(1\sigma g)^2(1\sigma u*)^2(1\pi u)^4(2\sigma g)^2$**, with an inversion of the **σ** and **π** levels compared to dioxygen. This corresponds to a triple bond N≡N, which is particularly stable (946 kJ/mol) and more stable than three single N-N bonds. This is why dinitrogen is very difficult to activate; certain bacteria are capable of fixing atmospheric nitrogen into organic matter, but they are rare.

4.3.1.1 Industrial Synthesis of Dinitrogen (N2)

Dinitrogen is a diatomic molecule composed of two nitrogen atoms. It is noted as N_2. Under normal temperature and pressure conditions, dinitrogen molecules form a colorless gas, making up 78% of the air. In the 21st century, dinitrogen is generally obtained by liquefaction of air, where it is the main constituent with a concentration of 78.06% by volume and 75.5% by mass, followed by fractional distillation.

4.3.1.2 Industrial Synthesis of Ammonia (NH3)

Ammonia is a chemical compound with the formula NH3NH_3NH3 (generic group of hydrogen nitrides). Under normal temperature and pressure conditions, it is a gas noted as NH3NH_3NH3 . It is produced industrially in large quantities by the Haber-Bosch process from dinitrogen and dihydrogen. This industrial gas is one of the most synthesized compounds in the world. Besides its common use as a refrigerant, it is used to synthesize many other compounds, including those widely used as fertilizers. This colorless gas is irritating, has a pungent odor, and burns the eyes and lungs.

$$\mathrm{N_2 + 3H_2 \longrightarrow 2\,NH_3} \qquad \Delta \mathrm{H}^0_{298} = -\,92{,}2\ \mathrm{kJ/mol}$$

4.3.1.3 Industrial Synthesis of Nitric Acid (HNO3)

Nitric acid is a chemical compound that is colorless and odorless in its pure form. Nitric acid is a highly caustic liquid, mainly used to make fertilizers. Nitric acid is involved in the production of nitroglycerin. It is very dangerous to health and can burn the skin upon contact. Inhaled vapors attack the respiratory system. The chemical formula for nitric acid is HNO_3.

Ostwald Process:

Commercial production of nitric acid is primarily done by the Ostwald process, carried out in three stages from ammonia **(NH_3)**

- First, ammonia is oxidized in the presence of a catalyst such as platinum-rhodium to form nitric oxide **(NO)** (a highly exothermic step).
- Then, nitric oxide is oxidized by oxygen **(O_2)** to produce nitrogen dioxide **(NO_2)**.
- Finally, nitrogen dioxide is dissolved in water to produce dilute nitric acid.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2\,(aq) + HNO_3\,(aq)$$

The nitric oxide produced is recycled, and nitric acid is concentrated by distillation to a maximum of 68% (the azeotrope of the nitric acid-water mixture). Higher concentrations are achieved by treatment with magnesium nitrate **($Mg(NO_3)_2$**. Overall, this process achieves a yield of 96%.

The global annual production of nitric acid (by different processes) is around 60 million tons.

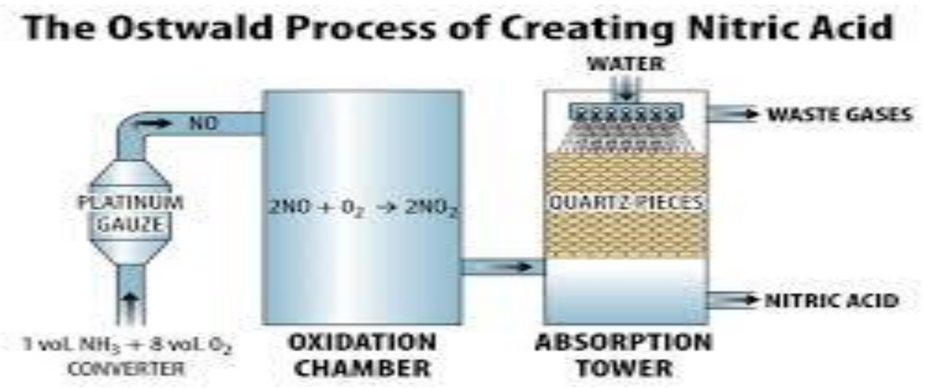


Figure 30 : Ostwald Process creating Nitric Acid

4.3.2 Phosphorus (P)

Phosphorus exhibits allotropy, appearing as white phosphorus, red phosphorus, violet phosphorus, and black phosphorus. The most stable form is white phosphorus.

4.3.2.1 Allotropic Forms of Phosphorus

Phosphorus has five crystalline forms and many amorphous phases. The most common allotropic forms are white and red phosphorus, but black and violet phosphorus also exist. All forms produce the same liquid and vapor of P4 (tetraphosphorus) molecules.

- **White Phosphorus**

  White phosphorus or tetraphosphorus is made up of $\mathbf{P_4}$ (4 P atoms, d(P−P)=225 pm). It is a waxy transparent solid (melting point = 44.2°C, boiling point = 280.5°C, density = 1.82 g/cm^3) that turns yellow in the presence of light. It is toxic, unstable, highly flammable, and pyrophoric (self-igniting) when in contact with air. White phosphorus is often stored in water as it is insoluble, though it dissolves in benzene, oils, carbon disulfide, and sulfur chloride.
- **Red Phosphorus**

  Red phosphorus is a thermodynamically stable amorphous allotrope of phosphorus (melting point = 600°C, density = 2.16 g/cm^3). It is less flammable than white phosphorus and non-toxic (the matchbox striker contains red phosphorus). It can be obtained by gently heating white phosphorus to around 240°C or by exposing it to sunlight. Red phosphorus can be converted back into white phosphorus at 260°C.
- **Violet and Black Phosphorus**

  Violet phosphorus (monoclinic crystal), known as Hittorf's phosphorus, is a polymer with a very complex structure containing cycles of 5 phosphorus atoms. Black phosphorus (orthorhombic crystal) is the most thermodynamically stable form and has a three-dimensional covalent polymeric structure (boiling point = 610°C).

4.3.2.2 Preparation of Phosphorus

Phosphorus is prepared by reduction in an electric furnace at about 1500°C from natural phosphate $\mathbf{Ca_3(PO4)_2}$. A mixture of coke (C) and silicon dioxide **(SiO_2)** is used as a reducing agent. The oxidation number of phosphorus changes from **+5** in $\mathbf{Ca_3(PO_4)_2}$ to **0** in $\mathbf{P_4}$.

$$\mathbf{2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow P_4 + 6\ CaSiO_3 + 10\ CO}$$

4.3.2.3 Synthesis of Orthophosphoric Acid(H3PO4)

In usual conditions, $\mathbf{H_3PO_4}$ is a solid (melting point = 42.35°C). When melted, the liquid is viscous (due to hydrogen bonding), easily dehydrates, and self-ionizes.

$$\mathbf{2\ H_3PO_4 \leftrightarrow H_4PO_4^{+} + H_2PO_4^{-}}$$

4.3.2.3.1 Different Types of Production Processes

Phosphoric acid can be synthesized through two different routes:

a) **Thermal Process:**

(abandoned due to high energy consumption):
Phosphorus prepared in an electric furnace at temperatures between 1200 and 1500°C is oxidized with coke and silica to produce phosphate anhydride, which is then hydrated into phosphoric acid according to the following reactions:

$$Ca_{10}(PO_4)_6F_2 + 8SiO_2 + 16\,C \xrightarrow{Heat} 8CaSiO_3 + 2CaF_2 + 16CO + 6P$$

$$P_2 + \frac{5}{2}O_2 \longrightarrow P_2O_5$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

b) **Wet Process:**

Phosphate ore is attacked with an acid (sulfuric acid H2SO4\text{H}_2\text{SO}_4H2 SO4). This process can be subdivided into two categories:

a. Single attack process → produces dihydrate gypsum.
b. Two-step attack process → produces hemihydrate or semi-hydrate gypsum

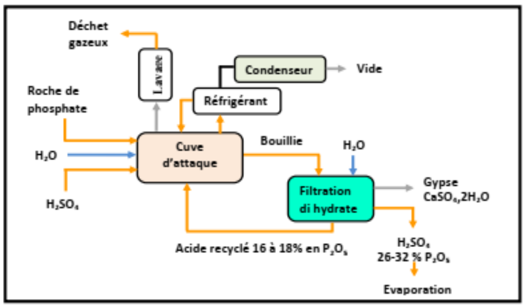


Figure 31: : Simplified diagram of the DH

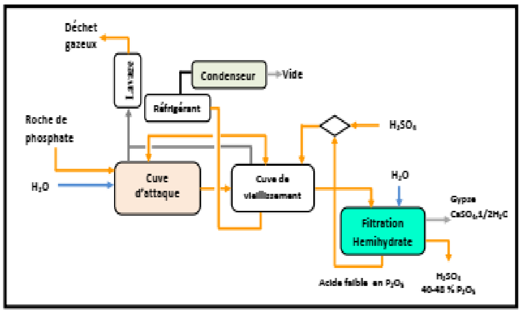


Figure 32 :Simplified diagram of the HH

In summary: The wet process is a cost-effective method for producing phosphoric acid for fertilizers, while the thermal process offers a higher purity product suitable for a wider range of industrial applications.

5 Chapter V Major Metallurgies

Historically, metals and alloys have been used for their ease of shaping—casting, hammering—and their hardness, for tools and weapons, and sometimes for their shine—jewelry, mirrors. Today, many other materials are used for these applications: ceramics, polymers, composite materials, but metals still play an important role.

In fact, the success of metallurgy lies in five words: the abundance of metals in the Earth's crust; their high malleability; the ability to modify their mechanical properties through thermomechanical treatments; the extraordinary mastery of many associated technologies; and finally, the electrical and thermal conductivity characteristic of metals and alloys, along with the magnetism of some of them.

5.1 Properties of Pure Metals

By "pure metal," we mean a "metallic crystal composed of a single element." Metals are rarely used in their "pure" form for two reasons:

1. They contain impurities from the original ores or introduced during the production process.
2. Alloys often have more interesting properties.

Figure 33 : Diagram of reactivite

Sometimes ultra-pure metals are produced at high costs for specific applications: scientific research, electronics.

Although the properties of pure metals do not correspond to the materials actually used, particularly in terms of electrical resistivity, they are often close enough to understand the choice of materials.

Metallurgy primarily occupies the secondary sector (transformation) of the economy, while the primary sector is limited to mining extraction.

There are distinctions between:

- **Primary Metallurgy**, which produces the first product that can be classified as "metal";
- **Secondary Metallurgy**, which refines the metal, purifies it, and gives it the chemical composition compatible with the desired properties;
- **Forming**, which creates semi-finished products such as sheets, bars, tubes, profiles, and cast pieces—this is the field of boilermaking;
- **Machining**, which, by material removal, gives the piece a precise shape.

5.2 Group of Alkaline Earth Metals- Group (IIA)

1. **Be** - Beryllium
2. **Mg** - Magnesium
3. **Ca** - Calcium
4. **Sr** - Strontium
5. **Ba** - Barium
6. **Ra** - Radium (radioactive element)
7.

5.2.1 General Characterization

- The elements of Group IIA have two electrons in their valence shell (hence the +2 oxidation state characteristic of the group).

5.2.1.1 Electronic Configuration: ns2

- Their position near the noble gases in the periodic table determines their tendency to give up two electrons, resulting in divalent ions with a noble gas configuration (except Be, which ionizes with difficulty).

5.2.1.2 Natural State

- **Be** is found in the Earth's crust as beryl (beryllium and aluminum metasilicate) **Be_3Al_2 [Si_6O_{18}]**.
- **Mg** is present in deposits as magnesite **($MgCO_3$)** and dolomite (a double carbonate of calcium and magnesium: **$MgCO_3 \cdot CaCO_3$**).
- **Ca** is found in limestone deposits ($CaCO_3$, calcium carbonate), dolomite, and gypsum **($CaSO_4 \cdot 2H_2O$).**

5.2.1.3 Chemical Reactivity

Reaction with H_2:

All alkaline earth metals (M) react with hydrogen to form hydrides:

$$M(s) + H_2(g) \rightarrow MH_2(s)$$

Reaction with O_2:

Formation of oxides:

By direct reaction with oxygen, all Group II_A elements form oxides:

$$2M + O_2 \rightarrow 2MO$$

Beryllium only reacts with O_2 in powder form. Otherwise, a thin layer of beryllium oxide (BeO forms on the surface of the metal, preventing further oxidation.

Alkaline earth metal oxides are basic (except BeO):

$$MO + H_2O \rightarrow M(OH)_2$$

Reaction with Air:

The oxidation of alkaline earth metals by air leads to a mixture of oxides and nitrides:

$$2M(s) + O_2(g) \rightarrow 2MO(s)$$
$$3M(s) + N_2(g) \rightarrow M_3N_2(s)$$

Reaction with Acids

- **Reaction with Dilute HCl:**

$$M + 2HCl \rightarrow MCl_2(aq) + H_2$$

- **Reaction with Dilute H_2SO_4:**

Beryllium and magnesium react with **H_2SO_4** similarly to HCl, forming colorless solutions of **BeSO4** and **MgSO4**.

Due to the insolubility of **$CaSO_4$**, **$SrSO_4$**, and **$BaSO_4$**, the reaction of calcium, strontium, and barium with dilute H_2SO_4 leads to the formation of a thin layer of insoluble sulfate on the surface of the metal, effectively stopping the reaction.

- **Reaction with HNO_3:**
  Beryllium requires special reaction conditions. For other metals (magnesium, calcium, strontium, and barium), the formation of reaction products is influenced by the concentration of HNO_3.
- **Dilute HNO_3:**

$$M + 2HNO_3 \rightarrow M(NO_3)_2 + H_2$$

- **Moderately Concentrated HNO_3:**

$$3M + 8HNO_3 \rightarrow 3M(NO_3)_2 + 2NO + 4H_2O$$

- **Concentrated HNO_3:**

$$M + 4HNO_3 \rightarrow M(NO_3)_2 + 2NO_2 + 2H_2O$$

5.2.2 Differences in Group (IIA) élements

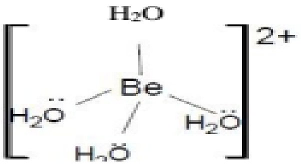
The first element in the group, beryllium, differs in properties from other elements. Beryllium has lower reactivity due to the formation of a BeO layer on its surface (similar to aluminum). While the chlorides of alkaline earth metals **(MCl_2)** are ionic (for Mg, Ca, Sr, and Ba), beryllium chloride **($BeCl_2$)** is covalent and is characterized by these features.

Formation of Ions in Aqueous Solution :

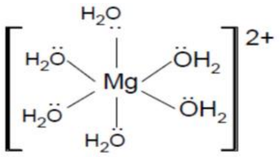
When ions form in solution **($[M(H_2O)_n]^{m+}$** water molecules form coordination bonds with the central metal ion. One of the unshared electron pairs on the oxygen atom in water bonds with an available orbital of the metal ion. The formation of such a bond releases energy, thus increasing the stability of the metal ion.

Example 1:

Formation of ions in solution: **$[Be(H2O)_4]^{2+}$**



Formation of ions in solution for magnesium: **$[Mg(H2O)_6]^{2+}$**



Electronic Configuration: : Mg : **$1s^2 2s^2 2p^6 3s^2$**

Magnesium ion (Mg2$1s^2 2s^2 2p^6$

- When hydrating Mg2+, the 3s, 3p, and 3d orbitals hybridize to form 6 sp^3d^2 hybrid orbitals. The maximum coordination number for Mg is 6, resulting in an octahedral geometry.

5.3 Group of Alkaline Metals - Group (IA)

- **Li** - Lithium
- **Na** - Sodium
- **K** - Potassium
- **Rb** - Rubidium
- **Cs** - Cesium
- **Fr** - Francium (radioactive element)

5.3.1 Electronic Configuration: ns1

- The elements in Group IA have one external electron (hence the characteristic +1 oxidation state). Positioned in the periodic table after the noble gases, the elements in this group have a strong tendency to lose their valence electron, thus achieving a noble gas configuration:

$$\mathbf{M \rightarrow M_{+} + 1e^{-}}$$

- Alkali metals are characterized by low ionization energies, which leads to their strong tendency to form ions and, therefore, ionic compounds.

5.3.2 Natural Sources

The elements of Group IA are mainly found as chlorides (in the Earth's crust and in seawater).

5.3.3 Physical Properties

- Low hardness (easy to cut)
- Silvery luster
- Low density
- Low boiling and melting points

5.4 Transition Metals (dx ; x=1-10)

Transition metals are considered elements with partially occupied d or f orbitals. This includes elements with atoms that have partially occupied d or f orbitals in their common oxidation states.

General Properties

- High hardness, malleability, and ductility
- Good conductors of heat and electricity
- Most of these elements have multiple oxidation states
- Their compounds display different colors depending on the oxidation state

5.4.1.1 Chemical Properties

- A characteristic feature of transition metals is their ability to form complexes due to their small volume, which allows them to be good electron acceptors.
- The coordination number is influenced by steric and electronic factors.
- Large-volume ligands will form complexes with a small coordination number, while complexes with smaller ligands and a central metal with a higher atomic radius will have larger coordination numbers.

Complex Formation in Transition Metals :

During complexation, ligands donate a pair of electrons, forming two-electron covalent bonds (coordination bonds) with the central atom. The ligand acts as a base, donating a pair of electrons to the central metal atom of the complex: **L : + M → [L : → M]**

5.5 Primary Metallurgy

As previously stated, most metals are naturally present in oxidized form, mainly as oxides or sulfides in ores (rocks).
Primary metallurgy involves, after the recovery of the ore (mining or quarrying), crushing the raw ore:

- **Crushing or grinding** !

The ore (large machines) Separating the different components of the rock and reducing the ore, which means removing oxygen from the metal.

- **Extraction Methods or Phase Separation:**

Magnetic separation: for ferrous metals (If the mineral has magnetic properties)

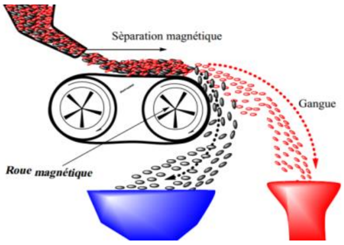


Figure 34 : Magnetic separation

- Using differences in density or buoyancy: decantation, centrifugation, filtration, flotation
- Dissolving one of the phases in an aqueous solution, called leaching:
    - Leaching with an acid (sulfuric acid for copper ore)
    - Leaching with a base (sodium hydroxide for aluminum ore)
- Reaction with a solid containing silica, producing a liquid called slag (for nickel ore)
- Gasification, reacting the metal oxide to transform it into gas (reaction of titanium ore with chlorine), followed by separation through distillation.

Once the metallic oxide is separated from the other parts of the rock, it can be reduced:

- By carbon monoxide produced from coal combustion (for iron and copper)
- By hydrogen gas (for nickel)
- By electrolysis — passing an electric current through a liquid (for aluminum).

  The process is called pyrometallurgy when heat is used, hydrometallurgy when an aqueous solution is used, and electrometallurgy when electric current is used.

5.6 Secondary Metallurgy

Secondary metallurgy involves purifying the obtained metal: degassing and removing impurities. Techniques used include:

- Vacuuming the molten metal to remove gases
- Adding substances to trap impurities in a different phase, which can be easily removed (slag floating on the molten metal)
- Bubbling air or pure oxygen (puddling) to oxidize certain impurities and trap them in slag.

C'est actuellement grâce aux divers traitements de métallurgie secondaire, évoqués dans les précédents paragraphes, que sont réalisées les opérations essentielles relatives à l'obtention des caractéristiques du produit final prévu :

qualité analytique du métal liquide : par la mise à la nuance et le contrôle de certains non-métaux

maîtrise de la quantité, de la dimension et de la composition des inclusions ;

réglage thermique, grâce au contrôle des pertes et à des actions de refroidissement (par ajout de ferrailles) ou de réchauffage du métal par l'utilisation d'énergie électrique (poche chauffante à arcs), ou chimique (aluminothermie).

Des modèles thermodynamiques et cinétiques peuvent être utilisés comme guide pour aider l'aciériste à choisir les conditions de traitement les mieux adaptées à l'élaboration de la plupart des nuances d'acier actuelles.

C'est sur la reproductibilité des résultats et l'obtention de teneurs en résiduels non métalliques de plus en plus faibles que devront porter les efforts dans le futur. Ceci devrait passer par une modélisation complète des réacteurs prenant en compte, non seulement les aspects thermodynamique et cinétique des réactions élémentaires, mais également les sites réactionnels et l'hydrodynamique dans le réacteur.

6 Chapter VI Coordination Compounds

Metals play a very important role in everyday life, comprising 90% of the periodic classification of elements. Their uniqueness lies in their d atomic orbitals, which grant them specific properties such as optical, magnetic, color, and conductivity characteristics. Transition elements and their compounds

6.1 General Definitions

A transition element is defined as an element, the element whose atomic state has a layer d (transition metals) or f (lanthanides, actinides) partially filled.

Example

Series 1: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Series 2 : Y Zr Nb Mo Tc Ru Rh Pd Ag Cd

Series 3: Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg

6.2 General Properties

Transition metals possess interesting properties for industry, including:

- They are good thermal and electrical conductors, with silver
- They can form alloys among themselves.
- They have a moderate oxidation rate
- They form numerous complexes.

Electronic Exception:

The 3d and 4s (or 4d and 5s) orbitals have close energies. We then observe a particularity in the order of filling. Electrons from the s orbital can pass into the d orbital, if the latter would be stabilized. The 3d orbitals then act somewhat like core orbitals.

Case of Chrome Cr (Z=24) [Ar] $4s^13d^5$ and the Case of Copper Cu (Z=29) [Ar] $4s^1\ 3d^{10}$

6.3 Ligands and Complexes

The manner in which ligands coordinate is called denticity. There are monodentate, bidentate, tridentate, etc., ligands. Monodentate ligands form a single metal-ligand bond, such as ammonia (ammine ligand), water (aqua ligand), or charged species like Cl^- (chloro ligand) or CN^- (cyano ligand).

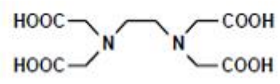
Bidentate ligands form two M-L bonds with the same or different central atoms. In the first case, the ligand is bidentate chelating, as in 1,2-diaminoethane or ethylenediamine $NH_2\text{-}CH_2$

Chelate Effect:

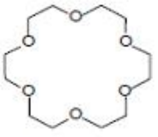
Chelation occurs when a multidentate ligand (with multiple donor atoms) forms all its bonds with a single central ion, which is then enclosed in a cyclic structure, as if held by pincers (from the Greek *chelatos* = pincers). When the element forms 5- or 6-membered rings with the chelating molecule, the resulting complex is generally very stable.

Note:

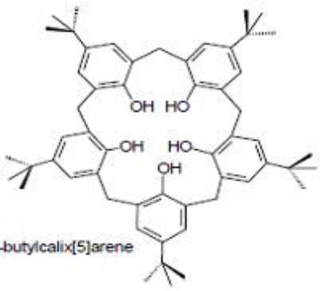
Chelation is a natural phenomenon. It occurs with the cobalt ion in vitamin B12, magnesium in chlorophyll, and iron in hemoglobin. Additionally, other types of ligands are known, such as polydentate ligands (like EDTA) and macrocyclic ligands.



acide éthylènediamine tétraacétique edta

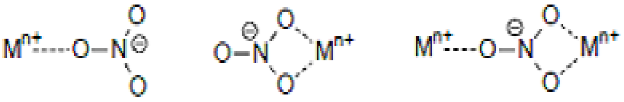


éther 18-couronne-6



p-tert-butylcalix[5]arene

Certains ligands se comportent différemment suivant leurs états. Par exemple le nitrate :



monodenté bidenté tridenté (pontant)

6.4 Nomenclature of Complexes

Nomenclature is important in coordination chemistry due to the existence of isomers. In 1970, the International Union of Pure and Applied Chemistry (IUPAC) established the following rules:

- To name the entire complex, the name of the anion is given first, followed by the cation.
- In the complex ion, the name of the ligand(s) precedes the name of the central metal atom.

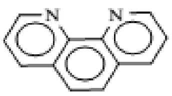
- The name of the ligand generally ends with "o" if the ligand is negative. If more than one ligand is present in the complex, they are named in alphabetical order, regardless of their number.
- A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) is used to indicate the number of each type of ligand.
- A Roman numeral or zero in parentheses is used to indicate the oxidation state of the central metal atom.
- If the complex ion is negative, the name of the metal ends in "ate."

Note: Brackets "[ ]" are used to enclose a complex ion or a neutral coordinated species. Some examples are provided below:

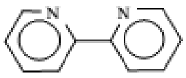
H_2O	aqua	$[Cu(H_2O)_4]^{2+}$	ion tétraaquacuivre(II)
NH_3	ammine	$[Ni(NH_3)_6]^{2+}$	ion hexaamminenickel(II)
CN^-	cyano	$[Ni(CN)_4]^{2-}$	ion tétracyanonickelate(II)
Cl^-	chloro	$[FeCl_4]^-$	ion tétrachloroferrate(III)
Br^-	bromo	$[AlBr_4]^-$	ion tétrabromoaluminate(III)
OH^-	hydroxo	$[Al(OH)_4]^-$	ion tétrahydroxoaluminate(III)
O^{2-}	oxo	$[ReCl_3O_3]^{2-}$	ion trichlorotrioxorhénate(VII)
$\underline{N}O_2^-$	nitro	$[Co(NH_3)_5NO_2]^{2+}$	ion pentaamminenitrocobalt(III)
CO	carbonyl	$[Ni(CO)_4]$	tétracarbonylnickel(0)
CH_3COO^-	acétato	$[Cu_2(CH_3COO)_4(H_2O)_2]$	tétra-μ-acétatodiaquadicuivre(II)
CO_3^{2-}	carbonato	$[Co(NH_3)_4CO_3]^+$	cation tetraamminecarbonatocobalt(III)
NO	nitrosyl	$[Fe(CN)_5NO]^{2-}$	anion pentacyanonitrosylferrate(II)

- **$[Ni(H_2O)_6]^{2+}$**: Hexaaquanickel(II) ion
- **$[PtCl_4]^{2-}$**: Tetrachloroplatinate(II) ion
- **$[Co(NH_3)_6]^{3+}$**: Hexaamminenickel(III) ion
- **$K_4[Fe(CN)_6]$**: Potassium hexacyanoferrate(II)

SO_4^{2-} sulphato $[Cu(en)(H_2O)_2SO_4]$ diaquaéthylènediaminesulphatocuivre(II)



1,10-phénantroline (phen) $[Fe(phen)_3]^{3+}$ ion tris(phénantroline)fer(III)



$[Ni(bipy)_3]^{2+}$ ion tris(bipyridine)nickel(II)

6.5 Coordination Geometry And Coordination Number

The wide variety of existing complexes is due to the variability in the number of metal-ligand bonds formed, or coordination number. The coordination number is variable and determines the geometry of the formed species. Structural studies have shown that the coordination number can range from 2 to 12. The situation becomes more complex when a given coordination number exhibits different geometries.

6.5.1 Coordination Number 2

This typically involves a (quasi) linear geometry. It is observed for central atoms with a d^{10} electron configuration, such as Cu(I), Ag(I), Au(I), and Hg(II). Examples include:

a. Dicyanoargentate(I) anion: $[Ag(CN)_2]^- \rightarrow [N\equiv C\text{-}Ag\text{-}C\equiv N]$
b. Dimethylmercury (II) molecule: $Hg(CH_3)_2 \rightarrow H_3C\text{-}Hg\text{-}CH_3$
c. Diamminecopper(I) cation: $[Cu(NH_3)_2]^+ \rightarrow [H_3N\text{-}Cu\text{-}NH_3]^+$

6.5.2 Coordination Number 3:

This is very rare and corresponds to either a trigonal planar or pyramidal geometry. It is often encountered with bulky ligands. Examples include:

d. Tricyanocuprate(I) anion: $[Cu(CN)_3]^{2-}$ (planar)
e. Trichlorostannate(II) anion: $[SnCl_3]^-$ (pyramidal)

6.5.3 Coordination Number 4:

This is very common. Complexes with coordination number 4 exhibit two possible arrangements: tetrahedral (Td) or square planar (D_4h). The tetrahedral arrangement is preferred for central atoms without d orbitals or with spherical symmetry, while the square planar geometry is favored by ions with a d^8 electron configuration. Examples include:

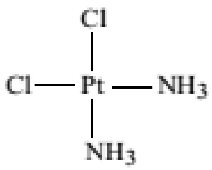
f. Tetrachloroferrate(III) anion: $[FeCl_4]^-$ (d^5, Td)
g. Tetraaquaberyllium(II) cation: $[Be(H_2O)_4]^{2+}$ (s^2, Td)
h. Tetracyanonickelate(II) anion: $[Ni(CN)_4]^{2-}$ (d^8, D_4h)
i. Diamminedichloroplatinum(II) molecule: $[Pt(NH_3)_2Cl_2]$ (d^8, D_4h)

2. The complex $[Pt(NH_3)_2Cl_2]$ can exhibit two possible geometries, depending on the positions of the ligands around the central atom:

3. Cis geometry: The same ligands are placed on the same side of the square.

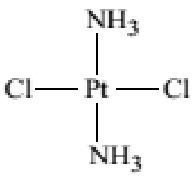
4. Trans geometry: The same ligands are positioned diametrically opposite.

5. These two geometries represent geometric isomerism for square complexes with the general formula MA_2B_2.



$$\begin{array}{ccc} & Cl & \\ & | & \\ Cl- & Pt & -NH_3 \\ & | & \\ & NH_3 & \end{array}$$

cis



$$\begin{array}{ccc} & NH_3 & \\ & | & \\ Cl- & Pt & -Cl \\ & | & \\ & NH_3 & \end{array}$$

trans

6.5.4 Coordination Number5 :

Coordination number 5 presents two limiting geometries: trigonal bipyramidal (D_3h), which is more common, or square pyramidal (C_4v). Experimentally, a deformed polyhedral structure is often observed, with an intermediate geometry between these two extremes. Examples include :

1. Pentachlorostannate(II) anion: $[SnCl_5]^{3-}$ (d^{10}, D_3h)
2. Pentacarbonyliron(0) molecule: $[Fe(CO)_5]$ (d^8, D_3h)
3. Pentacyanonickelate(II) anion: $[Ni(CN)_5]^{3-}$ (d^8, C_4v)

6.5.5 Coordination number 6 :

is the most common, typically corresponding to an octahedral geometry (Oh), though less commonly, a trigonal prismatic geometry may be observed. Examples include:

- Hexaaquafer(II) cation: $[Fe(H_2O)_6]^{2+}$ (d^6, Oh)
- Hexaamminenickel(II) cation: $[Ni(NH_3)_6]^{2+}$ (d^8, Oh)
- Hexacyanoferrate(III) anion: $[Fe(CN)_6]^{3-}$ (d^5, Oh)

6.6 Stability of Complexes

Several factors influence the stability of a given complex. These include factors related to the nature of the central metal ion (such as its charge density and electronic structure) and those related to the nature of the ligands.

6.6.1 The Metal Ion

6.6.1.1 Electronic Density

The electronic density can be represented by a theoretical model based on interactions between atomic orbitals.

6.6.1.2 Electronic Structure

The electronic structure of the metal ions plays a key role in determining the stability of complexes. For divalent metals, the Irving-Williams series is a well-known example and can be explained using the ligand field theory. There is a relationship between the nature of the donor atoms and the metal ion. Based on this, an empirical classification of metal ions was established by Ahrland et al. (1958) and

Schwarzenbach (1961), based on their affinity for different ligands. They proposed three groups (or classes):

- Class a : Includes cations with a noble gas-like electron configuration (e.g., Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}). These ions have low polarizability, high electropositivity, a small ionic radius, a high positive charge, and tend to form ionic bonds. Their affinity order with some donor groups is:

Example: $O^{2-} > F^- > Cl^- > Br^-$.

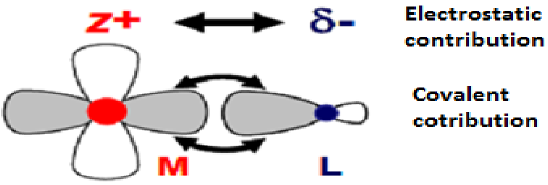
- Class b: Includes cations with a filled d-orbital configuration (18-electron rule), such as Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+}. These ions have opposite characteristics to class a, forming mainly covalent bonds, with a reversed affinity order.
- Class c: This class has intermediate characteristics between class a and b, including transition metals such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}.

These ideas were further developed by Pearson (1963) in the Hard and Soft Acid-Base (HSAB) theory, which classifies metal ions (acids) and ligands (bases) as hard or soft. According to this theory

- Hard acids prefer to bind with hard bases, and soft acids prefer to bind with soft bases.
    - Example: Aluminum-fluoride complexes are stable (F^- is a hard base, Al^{3+} is a hard acid), while mercury-fluoride complexes are less stable (Hg^{2+} is a soft acid).

6.6.2 Coordination Bond

The coordination bond results from two complementary contributions: an electrostatic contribution and a covalent contribution.



6.6.2.1 Electrostatic Contribution

This results from the attraction between the positive charge of the cation and the negative charge (or partial negative charge) carried by the donor atoms of the ligands. The intensity of this interaction depends on the size of the cation (given by its ionic radius, rir_iri) and its charge zzz. The charge density is defined by the ratio (z^2/ri), and this parameter is decisive for the strength of the interaction.

6.6.2.2 Covalent Contribution

This is associated with the overlap between the atomic orbitals of the metal and the molecular (or atomic) orbitals of the ligands.

6.7 Ligands

6.7.1 Nature of Donor Atoms

In the HSAB theory, ligands (coordinating species) are classified as hard or soft bases.

a) Hard bases generally have low polarizability, high electronegativity, negative charge, small size, and tend to form ionic bonds. Examples include H_2O and OH^-.

b) Soft bases exhibit opposite characteristics, such as higher polarizability and tend to form covalent bonds. Examples include R_2S, RSH, and I^-.

6.7.2 Chelate Effect

In general, the stability of complexes is significantly increased by chelation. This effect is most pronounced for coordination numbers 5 and 6, and it becomes weak or negligible for higher coordination numbers.

6.7.3 Size and Number of Rings

Generally, the greater the number of rings formed, the higher the stability of the complex. For example, stability increases when moving from ammonia (NH_3, no rings) to ethylenediamine (one ring), and then to diethylenetriamine (two rings).

6.7.4 Acid-Base Properties of the Ligand

Metal ions are considered Lewis's acids (electron acceptors), and the complexation of a metal ion by a ligand is similar to the neutralization of a base by an acid. Most ligands are the conjugate bases of acids, and generally, the higher the pK_a of the base, the greater the stability of the metal complex. While this correlation holds in many cases, there are exceptions.

6.7.5 Resonance

Resonance increases the stability of complexes. For resonance to occur, the complex must have a planar or nearly planar structure, as this allows for a greater domain for delocalized electrons, thereby enhancing stability. This is the case with porphyrins.

6.8 Crystal Field Theory

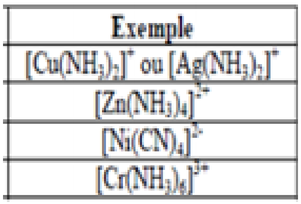
6.8.1 Valence Bond Theory (Pauling)

In terms of valence bond theory, the formation of a complex involves a reaction between Lewis bases (the ligands that donate electron pairs) and a Lewis acid (the metal or metal ion, which has empty orbitals), resulting in the formation of a covalent coordination bond (or dative bond).

This model uses the hybridization of the transition metal ion's nd, (n+1)s, (n+1)p, and (n+1)d orbitals to explain the structures and magnetic properties observed in complexes. Some common examples of hybrid orbitals formed according to the VSEPR theory and their corresponding complex geometries are shown in the following table:

Tableau 8: example of hybrid orbitals

Coordination number	Geometry	Hybrid Orbitals
2	Linear	(sp) or (ds)
4	Tetrahedral	sp^3 or (d^3s)
4	Square Planar	dsp^2
6	Octahedral	d^2sp^3 or sp^3d^2



Exemple
$[Cu(NH_3)_2]^+$ ou $[Ag(NH_3)_2]^+$
$[Zn(NH_3)_4]^{2+}$
$[Ni(CN)_4]^{2-}$
$[Cr(NH_3)_6]^{3+}$

In some cases, empty **4d atomic orbitals** can participate in the hybridization to satisfy the observed geometry and magnetic moment. An example is **Fe^{3+} (d^5)**, which exhibits two types of hybridization depending on the ligand environment and other factors.

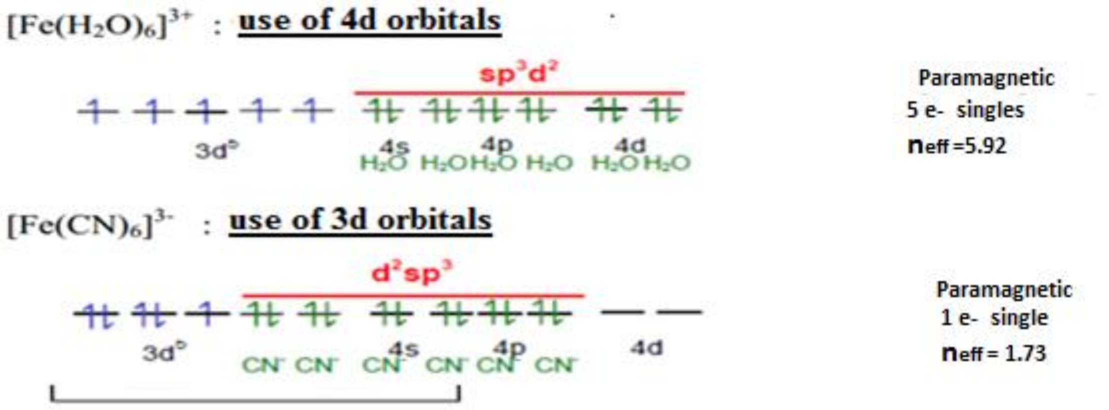


Figure 35 Type of Hybrdization in ligand environment

6.8.2 Examples of Hybridization in Fe^{3+}

1. d^2sp^3 hybridization: Leads to an octahedral geometry, common for many Fe^{3+} complexes where six ligands coordinate around the metal center.

2. sp^3d hybridization: Results in a trigonal bipyramidal geometry, observed in complexes with five coordinating ligands.

This explanation provides insight into the bonding, geometry, and magnetism of transition metal complexes, complementing crystal field theory for understanding the electronic structures of these species.

Principle of Crystal Field Theory (CFT):

Crystal Field Theory (CFT) is a theory that describes the electronic structure of transition metal complexes. These compounds are mostly coordination complexes or organometallic complexes. This model helps explain their magnetic properties, spin states, hydration enthalpies, and colors. However, it does not explain the bonding mode. The theory was developed by physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s. Later, it was combined with molecular orbital theory, giving rise to the more complex ligand field theory, which better describes the metal-ligand bonding within transition metal complexes.

6.8.3 Shape of d Orbitals and Lifting of Degeneracy

Like p orbitals, the shape of d orbitals is far from spherical symmetry. It is determined by the geometry of the electron cloud. There are five d orbitals:

- dxy, dxz, dyz, dx^2-y^2, and dz^2 (with reference to the Oxyz axes), or
- d-2, d-1, d0, d1, and d2 (in reference to the magnetic quantum number m, where m = -2, -1, 0, 1, 2).

These are directional orbitals formed by four lobes, except for the dz^2 orbital.

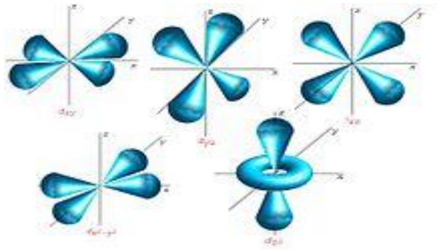


Figure 36 : Representation of the Five d Orbitals

This theory is a hybrid, borrowing from both classical electrostatic theory and quantum theory. The interactions are described in terms of the repulsion between the electrons present in the d orbitals of the transition metal element and the electron pairs from the ligands. In this model, ligands are considered as point charges, and the transition metal element is characterized solely by its d orbitals and the electrons they contain. The main objective is to describe the electronic configuration or electronic structure of a complex, focusing exclusively on the electrons present in the d orbitals.

6.8.4 Lifting of Degeneracy

The lifting of the degeneracy of the five d orbitals occurs due to the lowering of symmetry when moving from a free metal ion state (with spherical symmetry) to a complexed state, which may have octahedral, tetrahedral, or other symmetries. In spherical symmetry (in the free ion state), the five d orbitals (which differ only by their magnetic quantum number, m) are degenerate, meaning they have the same energy. In a multi-electron atom, energy depends only on the principal quantum number **n** and the secondary quantum number **l**. However, in lower symmetry, such as octahedral symmetry, this degeneracy is broken.

6.8.4.1 Lifting of Degeneracy in Octahedral Symmetry (Oh)

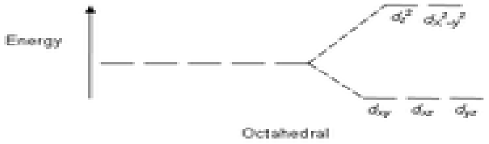


Figure 37 Degeneration inoctahedral symetry

In octahedral symmetry, the five d orbitals split into two different energy levels:

t2g level, which includes the dxy, dxz, and dyz orbitals, and **eg level**, which includes the **dx²-y²** and **dz²** orbitals.

This can be formally demonstrated using group theory, from which the labels t2g and eg are derived. The t2g orbitals have lower energy compared to the eg orbitals because, according to the electrostatic hypothesis, the interaction between the dx²-y² and dz² orbitals (which are aligned along the axes) and the electron pairs from the ligands is repulsive. In contrast, the dxy, dxz, and dyz orbitals, which are not directly aligned with the ligands, experience less repulsion.

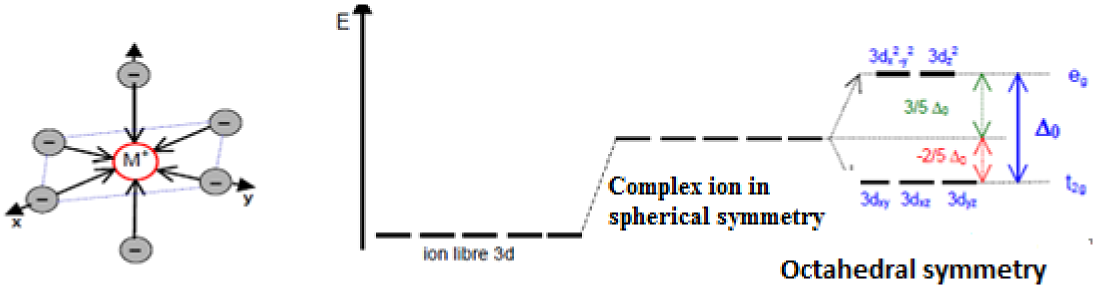
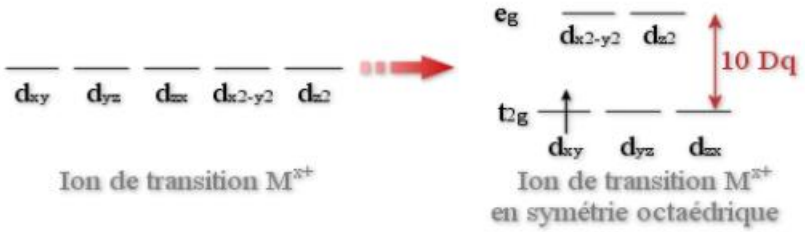


Figure 38 Detailed degeneration in octahedral symetry

In this case, the t2g orbitals lower their energy, becoming more stable, and this stabilization corresponds to -2Δo/5 per electron. On the other hand, the energy of the eg orbitals increases, with the destabilization corresponding to +3Δo/5 per electron.

For example, if we assume that the transition ion contains only one d electron (d^1 configuration), this electron will occupy one of the three t2g orbitals (which are identical in terms of symmetry) in order to minimize its energy.



6.8.4.2 Lifting of Degeneracy in Tetrahedral Symmetry (Td)

Tetrahedral symmetry, like octahedral symmetry, is a form of cubic symmetry, but it lacks a center of inversion. Group theory shows that the five d orbitals split into two levels labeled **e** (for the **dx^2-y^2** and **dz^2** orbitals) and **t2** (for the other three orbitals: **dxy**, **dxz**, and **dyz**). The lifting of degeneracy corresponds to the energy gap **Δt** (the splitting energy for d orbitals in tetrahedral symmetry), which separates the **e** and **t2** orbitals.

The labels **e** and **t2** in tetrahedral symmetry differ from **eg** and **t2g** in octahedral symmetry by the absence of the subscript **g** (gerade), which indicates parity with respect to the center of symmetry, a center that is absent in tetrahedral symmetry. The **e** energy level is lower than the **t2** level because, in tetrahedral symmetry, the ligands do not point directly along the axes, as they do in octahedral symmetry.

Thus, the energy diagram in tetrahedral symmetry is the inverse of that in octahedral symmetry. In tetrahedral complexes (tetrahedral field), the ligands are positioned between the x, y, and z axes (occupying four vertices of a cube, as shown in the figure below).

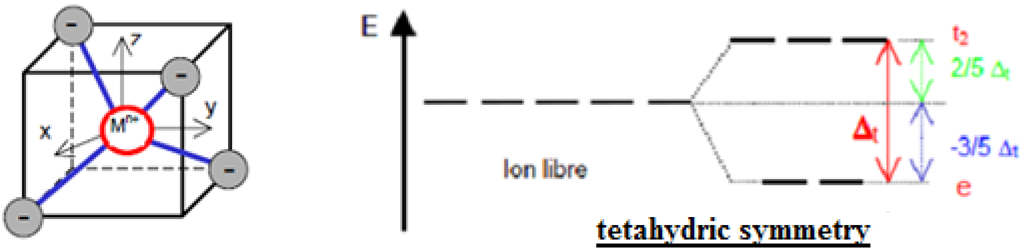


Figure 39 Degeration In tetrahedral symmetry

In tetrahedral symmetry, the stabilization corresponds to -3Δt/5 per electron for the e orbitals. On the other hand, the dxy, dxz, and dyz orbitals (degenerate as t2 orbitals) are destabilized, with a destabilization of +2Δt/5 per electron.

In the case of a tetrahedral field, the splitting energy (Δt) is smaller than in the octahedral field. For the same ligand and the same M-L distances, the ratio of the two splitting values is Δt = 4/9 Δo.

Note: In a spherical complex, the energy of the d orbitals is taken as the energy reference point (zero energy). In an octahedral complex, the t2g orbitals are lower in energy by 4 Dq, while the eg orbitals are higher in energy by 6 Dq.

6.8.4.3 Lifting of Degeneracy in Square Planar (D4h) Symmetry

Square planar (D4h) symmetry can be viewed as a reduction of **Oh symmetry** due to a deformation along the z-axis (Oz). Group theory shows that the five d orbitals split into three energy levels. This can be intuitively understood from the **Oh symmetry energy diagram**, where axial symmetry reduction causes the degeneracy of the **dx^2-y^2** and **dz^2** orbitals to be lifted. The **dz^2** orbital is less destabilized than **dx^2-y^2** because the unfavorable interaction between **dz^2** and the two ligands along the Oz axis decreases as the ligands move farther away, unlike those in the Oxy plane.

Thus, the electronic structure in D4h symmetry consists of:

A three-fold degenerate level for the dxy, dxz, and dyz orbitals.

A separate level for the dz^2 orbital.

Another separate level for the dx^2-y^2 orbital.

The degree of destabilization of the five d orbitals and the lifting of degeneracy depends on the shape and symmetry of the complex. This is quantified by the **crystal field energy** (denoted as 10 Dq), which represents the energy difference between the groups of orbitals (**dx^2-y^2** and **dz^2**) and (**dxy**, **dxz**, **dyz**). This crystal field energy is typically measured by **optical spectroscopy**.

6.8.5 Comparison of Different Symmetries

When comparing two different symmetries, such as **octahedral symmetry** (Oh) and **tetrahedral symmetry** (Td), the crystal field splitting differs due to the arrangement of ligands and the interaction with the metal center.

6.8.5.1 Other Symmetries

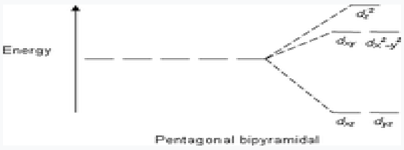
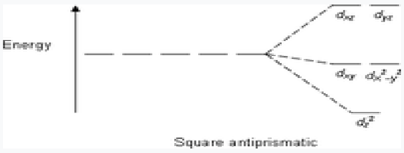
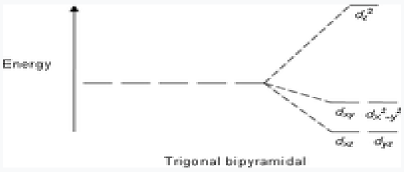
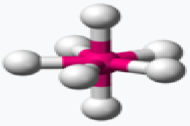
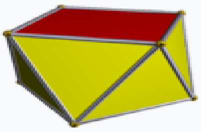
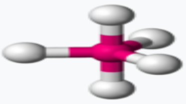
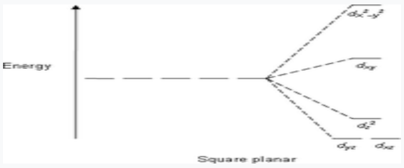
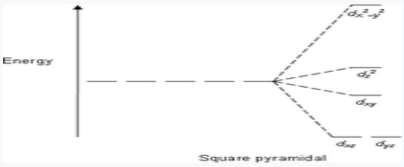
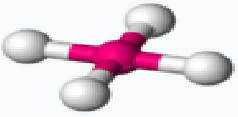
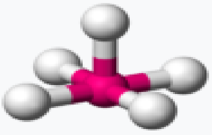
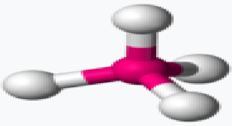
Other symmetries can also be analyzed in a similar manner, using group theory to determine how the degeneracy of the five d orbitals is lifted. In most practical cases, the three symmetries **Oh**, **D4h**, and **Td** account for the majority of observed complexes.

For rarer symmetries such as:

- Pentagonal bipyramidal
- Square antiprism
- Trigonal bipyramidal

Energy diagrams for these symmetries can be derived, although these geometries are encountered less frequently.

Tableau 9 Comparison of different symmetries

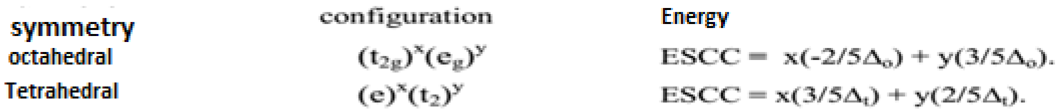
Pentagonal Bipyramid	Square Antiprism	Trigonal Bipyramid
		
		
Square Planar	**Square Pyramidal**	**Tetrahedral**
		
		

Specific Case: The perturbation of d atomic orbitals is different in the case of the electrostatic field for square-based bipyramid when the two axial ligands are farther away (or closer) than the four equatorial ligands. In this case, there is an additional splitting of degeneracy compared to the octahedral field: this is the Jahn-Teller distortion or effect.a

6.8.6 Calculation of Crystal Field Stabilization Energy (CFSE)

For each electronic configuration, we can associate a crystal field stabilization energy (CFSE). It corresponds to the energy gain or loss of the ion in octahedral symmetry compared to spherical symmetry.

The magnitude of stabilization depends on the number of electrons and their distribution in the orbitals (weak field, strong field). CFSE can be deduced as follows:



symmetry	configuration	Energy
octahedral	$(t_{2g})^x(e_g)^y$	ESCC = $x(-2/5\Delta_o) + y(3/5\Delta_o)$.
Tetrahedral	$(e)^x(t_2)^y$	ESCC = $x(3/5\Delta_t) + y(2/5\Delta_t)$.

In general, a metal complex always adopts the lowest energy configuration.

For the **d³** configuration in an octahedral field, all electrons are placed in the **t2g** orbitals, resulting in:

CFSE = -6/5Δo

But for four electrons, the filling of the d orbitals can occur in two ways:

- **Strong field**: If the field is strong, the fourth electron is placed in the t2gt_{2g}t2g orbital, requiring the pairing of two electrons. The energy gain is reduced by the pairing energy PPP. In this case, the energy gain will be:

CFSE -8/5 Δo + P.

- Weak field: If the field is weak, the electronic configuration will be

  t2g3eg1t_{2g}^3e_g^1t2g3eg1, and the stabilization energy will be:

CFSE = -3/5Δo.

where p is the number of electron pairs.

Filling the orbitals in two different ways is possible up to the 7th electron. The following table summarizes the stabilization energies for a weak and strong octahedral field compared to the spherical field for all configurations of the d-block. It can be observed that the most stabilized configurations are d^3 and d^8 in a weak field, and d^6 in a strong field. On the other hand, the d^0, d^5, and d^{10} configurations show no stabilization effect.

For a **d¹ electronic configuration** in an octahedral

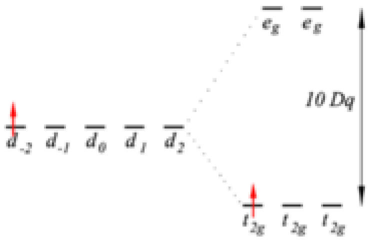


Figure 40 : Electronic configuration of an octahedral d1 complex

In an **octahedral complex**, the d-electrons of the metal center experience a splitting of energy due to the surrounding ligands, which creates a separation between the t2g and eg orbitals.