9th Course of Chemistry 1

The Chemical Bond

Introduction

When 2 atoms approach each other, there is an electronic rearrangement that leads to the formation of a molecule and consequently to a chemical bond.

The term chemical bond refers to the interactions that occur to keep the atoms together in a stable molecule.

The electrons involved in chemical bonds are the electrons in the outermost (valence) shells of the atoms. The energy of the formed molecule is lower than the sum of the energies of the atoms that gave rise to it.

$$\mathbf{A + B \longrightarrow A\text{-}B}$$

$$E_{AB} < E_A + E_B$$

The difference $E_{AB} - (E_A + E_B) =$ the energy of the chemical bond

Several types of bonds are distinguished:

1. *Interatomic bonds:*
   a - Covalent bond
   b - Ionic bond

2. *Intermolecular bonds*
   a - Van der Waals bond
   b - Hydrogen bond

3. *Metallic bond*
   This bond is fundamentally not different from the interatomic bond.

Definition.

1- Valence - valence electron - valence shell

- ✓ ***Valency*** is the number of covalent bonds that an atom can form.
- ✓ ***Valence electrons*** are the electrons in the outermost shell, known as the valence shell, of the atom.

2- Octet rule

- ✓ A covalent bond between 2 atoms A and B (identical or not) results from the sharing of 2 valence electrons.
- ✓ Each atom thus acquires the electron configuration of a noble gas (ns^2np^6), this is the octet rule.

- ✓ This means the atom will be surrounded by 4 pairs of electrons (either free or bonded).
- ✓ From the 3rd period onwards, atoms can be surrounded by more than 4 pairs of electrons (e.g. Si, Cl).

2- Lewis formula

- These are the formulas in which all the valence electrons of the bonded atoms are shown.
- A pair of electrons, whether shared (bonding pair) or not (non-bonding pair), is represented by a dash **(-)** or by 2 dots **(:)**

3- Interatomic bonds:

a - Covalent bond

a-1. Single covalent bond : This is the sharing of a pair of electrons between 2 atoms.

Example: diatomic molecules

H_2 : 1H: $1s^1$ un électron de valence

$H^{\bullet} + H^{\bullet} \longrightarrow$ **H : H** Doublet

$\longrightarrow$ **H — H**

b- Model of the covalent bond

The single covalent bond is a bond in which two single electrons are shared by two atoms.

It is therefore a sharing by two atoms of two of their electrons.

The shared electrons belong to both atoms at the same time, which corresponds to a gain of one electron for each atom. The covalent bond helps to keep the two atoms together very strongly: the covalent bond is called a strong bond because it takes a lot of energy to break it.

- *The covalent bond is represented by a line*.
- If two atoms share a single covalent bond, it is called *a single bond*.
- If two atoms share two covalent bonds, it is called *a double bond*.
- If they share three covalent bonds, it is called *a triple bond*.
- *Double bonds* are more stable and stronger than *single bonds*. *Triple bonds* are even more stable.

Note: electrons that don't participate in the bond are called *non-bonding electrons* or *non-bonding doublets.*

To facilitate the understanding of chemical bonding, *Lewis representation* is used. The representation is the clearest way to represent the bonds between molecules.

This representation was developed by Gilbert Lewis, an American physicist and chemist, in 1916.

Lewis Representation

- In Lewis representation, each atom is noted by its atomic symbol. Lewis representation only focuses on the electrons in the outer shell.
- Valence electrons are represented by dots.
- The first four electrons in the outer shell are noted by dots placed around the atoms. Since these electrons are alone, they are called lone pairs.
- Electrons can pair up with these lone electrons to form electron pairs. These pairs of electrons are represented as a line.
- Lone electrons seek to pair up together so that the outer shell is as stable as possible, saturated with 8 electrons.
- In this example, we can see that the first four elements have 4 lone electrons. (Li, Be, B, C but also Na, Mg, Al, Si).
- The following electrons are distributed to form pairs around the element.

The elements in the rare gas column (far right) have 8 peripheral electrons associated 2 by 2 in the form of 4 electron pairs: there are no lone electrons; they are inert or less reactive because their valence shell is saturated.

Note: Elements with the same number of valence electrons share the same Lewis representation.

Duet and Octet Rule

Atoms tend to seek maximum stability and try to acquire a complete electron shell, which is why they follow the *Duet or Octet rule*.
In simple terms, atoms all want to have the configuration of the nearest noble gas where all the lone electrons are paired. To achieve this, atoms follow.

the octet rule:

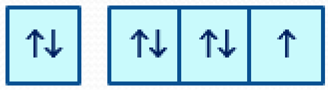
According to the Duet rule, an atom or ion is stable if its outer shell is K and has two electrons.
According to the octet rule, an atom or ion is stable if its outer shell L or M has 8 electrons.
To follow the Duet or Octet rule, an atom can gain or lose electrons to become an ion, but it can also form a covalent bond with another atom.

Note: There are, however, exceptions to the octet rule: atoms may have more or less than 8 electrons in their peripheral shell.

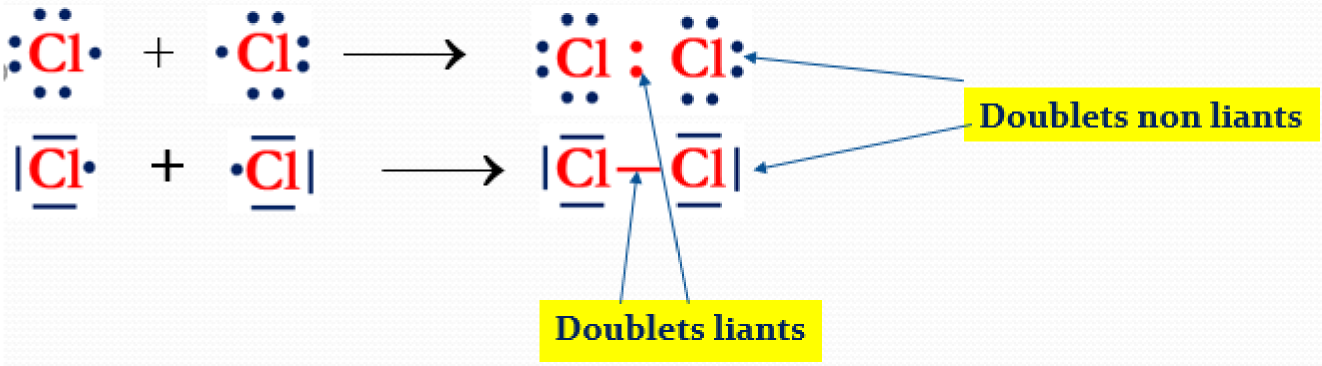
Example:

- Cl_2 la liaison implique des atomes à plusieurs électrons,

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



7 électrons de valence 3 doublets et un électrons de valence



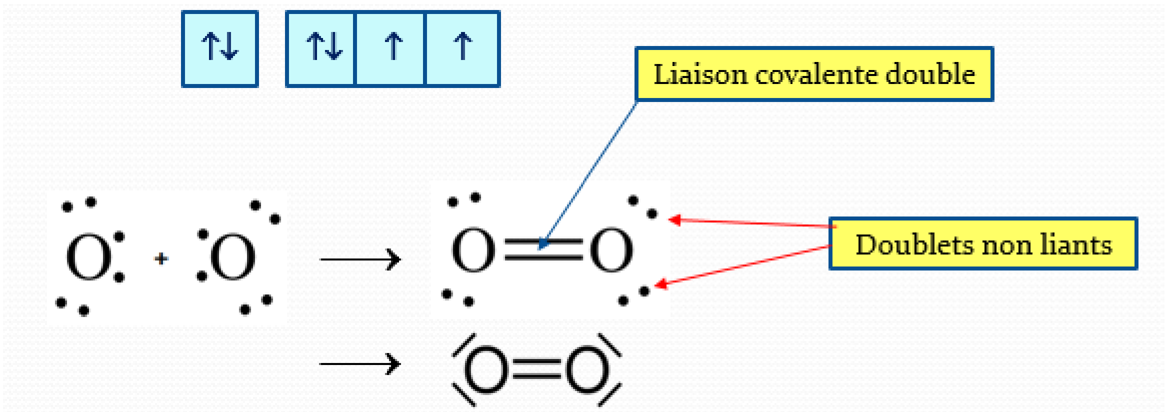
Polyatomic molecules:

Atoms are arranged side by side. The single atom or the least electronegative atom is often the molecule's central atom.

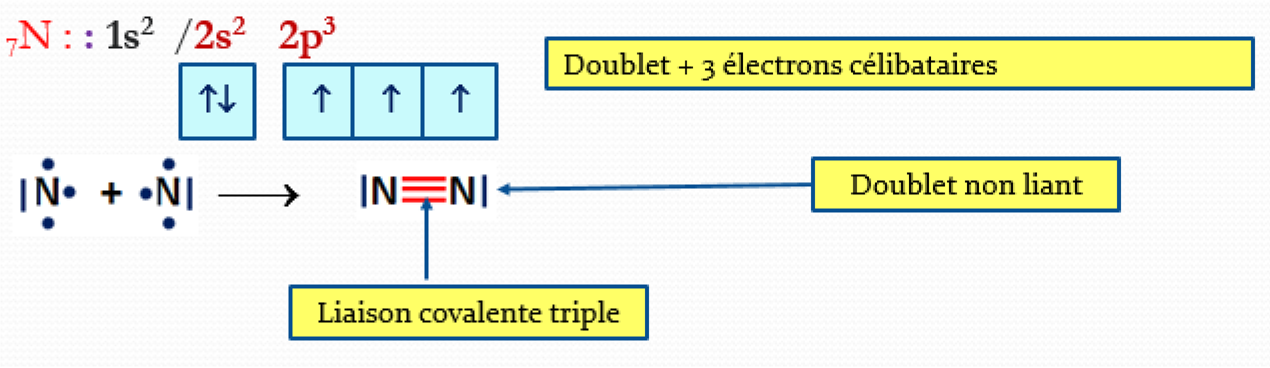
Double covalent bond : This results from the pooling of 2 pairs of electrons between 2 atoms.

Examples: O_2

$_8O$: : $1s^2$ / $2s^2$ $2p^4$

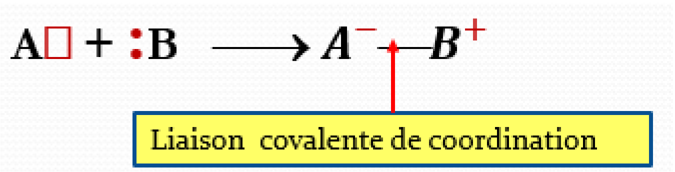


Triple covalent bond : It results from the sharing of three pairs of electrons between 2 atoms. Example of N_2 nitrogen.



Coordinate covalent bond (dative bond) (تساهمية) (تساندية)

• The coordination bond represents a particular type of chemical bond, and even a particular type of covalent bond. Formerly, the coordination bond was also called "dative bond", but the expression, even if it is still considered equivalent, is no longer recommended today. • *Bond between two atoms in which the shared electron pair comes from only one of the two bonded atoms*.



Examples of coordination bonds :

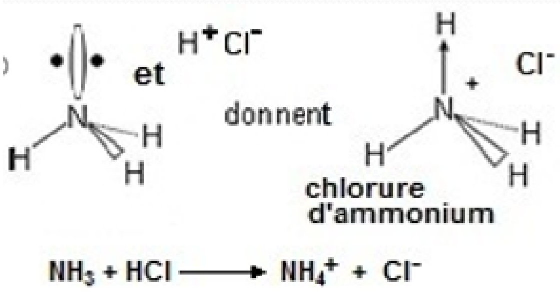
Here are two examples of coordination bonds:

1. The N-B bond in the compound $\mathbf{H_3N\text{-}BF_3}$;
2. the bonds between the protons **(H+)** and the nitrogen anion ($\mathbf{N_3^-}$) of the ammonium ion (NH_4^+).

Coordinate covalent bonds are mentioned when a *Lewis base* (electron donor) provides a pair of electrons to a *Lewis acid* (electron acceptor) to form an adduct. The process of forming a dative bond is called coordination, hence its name. The electron donor acquires a positive charge, while the electron acceptor acquires a formal negative charge.

Examples of coordination bonds

In a classical manner, any compound containing a pair of non-bonding electrons can form a coordination bond. The bond in various chemical compounds can be described as a coordination covalent bond (intermolecular NH3 or intramolecular CO): N: donor and H: acceptor.



l'ion ammonium (NH_4^+), peut être décrit comme NH_3 qui dispose d'un doublet libre et joue le rôle de base de Lewis et qui en présence d'un proton, donne un adduit (liaison de coordination **inter moléculaire**). C'est aussi NH_4^+ comprenant quatre liaisons covalentes de coordination virtuelles entre les protons (ions H^+) et le trianion azote N^{3-}.

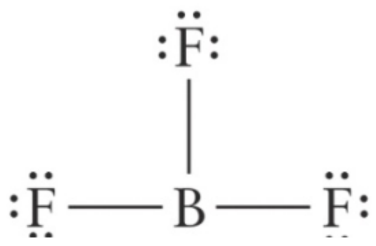
Carbon monoxide (CO) can be considered to present a coordination bond and two covalent bonds between the carbon and oxygen atoms. This very unusual description illustrates the flexibility of this type of description. Be aware that here, carbon is the electron acceptor and oxygen is the electron donor, contrary to what one might expect considering their respective electronegativity (C = 2.2 and O = 3.44).

Coordination bonds are commonly found in living molecules that contain a metallic component, such as chelates, molecules interacting with DNA (Zinc), and all pyrrole-based compounds like hemoglobin, myoglobin, or phytochrome. These coordination bonds are crucial for carrying out their biological functions.

Note: The concept of coordination bonds is frequently used to describe coordination complexes, especially those involving metal ions. In such complexes, several Lewis bases donate their "free" electron pairs to another metal cation lacking them, which acts as a Lewis acid and accepts the electrons. This forms coordination bonds, resulting in a compound called a "coordination complex," with the electron donors referred to as ligands.

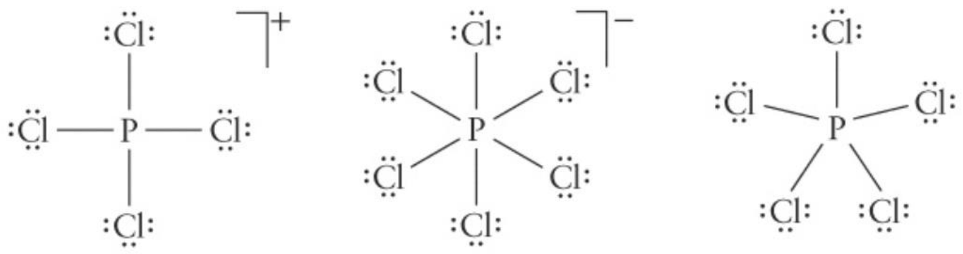
Exception to the Octet Rule

1. **1.** Incomplete Octet (Compounds formally containing fewer than 8 valence electrons) It concerns some elements of the 2nd period (B, Be,..) Example: BF3 boron is surrounded by 6 electrons.



2. **2.** Extension of the Octet Involvement of empty p or d orbitals: extended valence shells, hypervalent compounds (compounds formally containing more than 8 valence electrons). It concerns some elements of the 3rd period (P, S,,) .

Example



(a) PCl_4^+ (b) PCl_6^- (c) PCl_5

Other examples: SF_6, ICl_2^-, PO_4^{3-}, I^{3-}

Formal Charges

Formal charges are fictitious charges assigned to the atoms of a molecule by arbitrary rules. In order to calculate these formal charges, the covalent bond is considered to be equally shared between the two atoms, each of which is assigned one electron. The formal charges are then calculated using the following formula.

The formal charge of an atom "i" in a Lewis formula is given by the relation:

$$C_f = N_v - (N_{nl} + \frac{1}{2} N_l) \quad \text{Or} \quad C_f = N_v - (D_l + 2D_{nl})$$

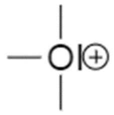
N_v: number of valence electrons
N_l: number of bonding valence electrons
N_{nl}: number of non-bonding valence electrons
D_l: bonding pairs
D_{nl}: non-bonding pairs

since: $D_l = 1/2\ N_l$ with D_l = number of bonds $\Rightarrow$ $\mathbf{C_f = N_v - (N_{nl} + D_l)}$

The sum of formal charges is always equal to the overall charge (z) of the structure.

Example :

- Formal charge of oxygen in $\mathbf{H_3O^+}$



${}_8O$: : $\mathbf{1s^2\ /2s^2\ \ 2p^4}$

N_v: number of valence electrons = 6

N_l: number of bonding valence electrons = 6, therefore $D_l = 3$

N_{nl}: number of non-bonding valence electrons = 2, therefore $D_{nl} = 1$

$C_f = N_v - (1/2\ N_l + N_{nl})$ $\Rightarrow$ $N_O = 6 - (1/2 \times 6 + 2) = 1$

or

$N_O = 6 - (3 + 2 \times 1) = 1$ $\Rightarrow$ $C_f = N_v - (D_l + 2\ D_{nl})$

Ionic Bond

Definition

A bond between two chemical elements is said to be ionic if the electronegativity difference between these two elements is significant, preventing them from sharing electrons. The formation of a covalent bond is no longer possible, as the electrons are no longer shared but entirely captured by the most electronegative atom, which becomes an anion, while the least electronegative atom loses one or more electrons, becoming a cation.

The so-called ionic bond is actually an attractive electrical interaction between cations and anions of an ionic solid.

Conditions for an Ionic Bond

For a bond to be ionic rather than covalent, there must be a sufficiently large electronegativity difference between the "bonded" elements. It is generally considered that a minimum difference of 1.7 is required.

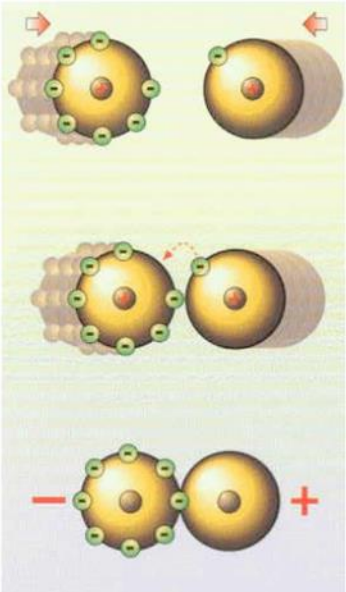
Examples of Ionic Bonds

- *The Fluorine-Hydrogen bond F-H*

Fluorine has an electronegativity of $\boldsymbol{\chi = 3.98}$, while *hydrogen's electronegativity* is only $\boldsymbol{\chi = 2.20}$. The electronegativity difference is $\boldsymbol{\Delta\chi = 3.98 - 2.20 = 1.78}$, which exceeds the threshold of 1.7. Therefore, the fluorine-hydrogen bond can be considered ionic.

The Chlorine-Sodium bond Cl-Na

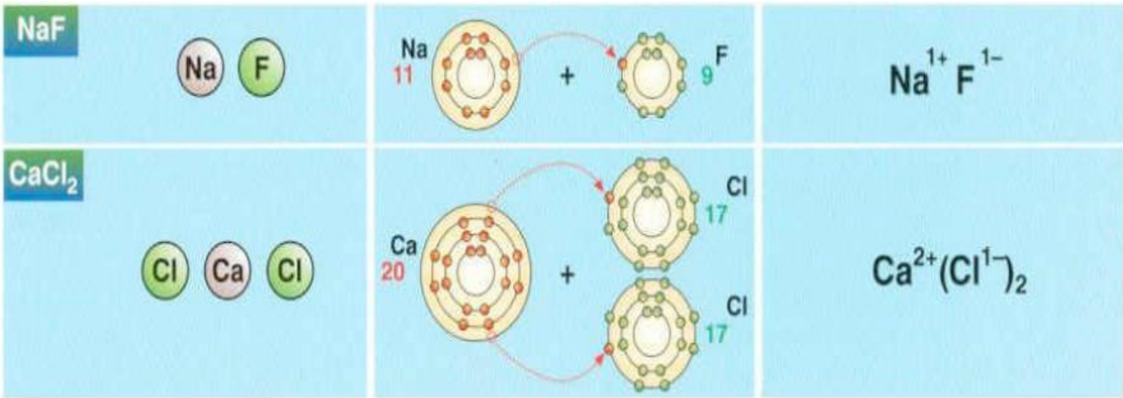
The electronegativity of chlorine is χ = 3.16 while that of sodium is χ = 0.93, which corresponds to a difference of $\Delta\chi = 3.16 - 0.93 = 2.23$, which is greater than the limit of 1.7. The Chlorine-sodium bond is therefore indeed an ionic bond.



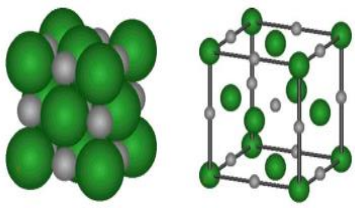
When the difference in electronegativity between the two atoms is sufficiently large, the first atom is able to capture valence electrons from the other atom. Thus, a positive ion and a negative ion are obtained. Given that opposite charges attract, the two ions are bound to each other. The atom that donates valence electrons has only a small number of electrons on its outermost shell and often eight electrons on the penultimate shell. When it donates its valence electrons, it thus achieves the configuration of a noble gas.

Remark

- In general, the elements in the first two columns of the periodic table (the alkali metals and the alkaline earth metals) always form ionic bonds with those in the penultimate column (the halogens). The first columns indeed contain the least electronegative elements, while the last ones (except for the noble gases) gather the most electronegative elements.

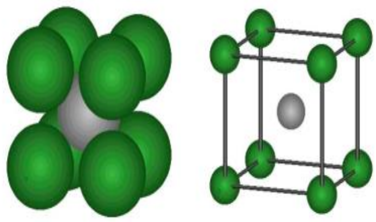


NaCl : chlorure de sodium



r_{Na+} = 99 pm
r_{Cl-} = 181 pm
La coordinence du sodium est de 6 et celle de l'ion chlorure est de 6.

CsCl : chlorure de césium



r_{Cs+} = 94 pm
r_{Cl-} = 181 pm
La coordinence du césium est de 8 et celle de l'ion chlorure est de 8

Comparison with other bonds and interactions

Ionic bonding is the strongest of the classical interparticle interactions, its intensity surpasses that of Van der Waals bonds (between permanent or instantaneous dipoles) as well as that of hydrogen bonds. It indeed corresponds to an electrostatic interaction (Coulomb force) between charged particles (ions) carrying overall charges (positive or negative) multiple of the elementary charge "e," while the other "bonds" correspond to intermolecular interactions between electric dipoles, i.e., globally neutral particles presenting a displacement of the centers of partial positive and negative charges.

Ionic solids

These are by definition solids made up of ions. These ions establish a crystalline lattice where cations and anions are stacked regularly (forming meshes). The attractive electrical interaction between anions and cations (constituting ionic bonds) is generally more intense than the repulsive interactions between ions of the same nature, which ensures the coherence of ionic solids.

Note : The predominance of attractive interactions results from the distribution of ions in the solid; overall, cations and anions are closer to each other than ions carrying charges of the same sign. Influence of Ionic Bonds on State Changes Ionic bonds are stronger than intermolecular interactions; therefore, it is necessary to provide ionic substances with more thermal energy to break these interactions: The state change temperatures of ionic compounds are generally higher than those of pure molecular substances. For comparison, here are some examples of melting temperatures (at a pressure of one atmosphere).
For molecular solids:

- Oxygen Melting Point = -218.8°C
- Ethanol Melting Point = -114°C
- Water Melting Point = 0.0°C
- Benzoic Acid Melting Point = 122.4°C
- Paracetamol Melting Point = 169°C For ionic solids:
- Potassium Bromide Melting Point = 734°C
- Sodium Chloride Melting Point = 800.4°C
- Sodium Carbonate Melting Point = 851°C
- Magnesium Sulfate Melting Point = 1124°C

Metallic Bond - Definition and Explanations

The metallic bond is a type of chemical bond, the bond that allows the cohesion of atoms in a metal.
A metallic bond involves a very large number of atoms (typically several million or more). These atoms share one or more electrons, called "free electrons" - it is these electrons that allow electrical conduction.
In comparison to the covalent bond, the free electrons can be seen as electrons delocalized throughout the metallic piece. The energy levels of the atoms can be described by the band theory.
The nature of the metallic bond is extensively studied in solid-state physics. The physical characteristics of metals such as malleability, ductility, and heat conductivity are explained by the nature of this bond.

Ionic Bond = Strong Metal + Strong Non-Metal

The strong metal, the strongest of all, is found on the far left and bottom of the Mendeleev's table: cesium. The strong non-metal, the strongest of all, is found on the far right and top: fluorine.

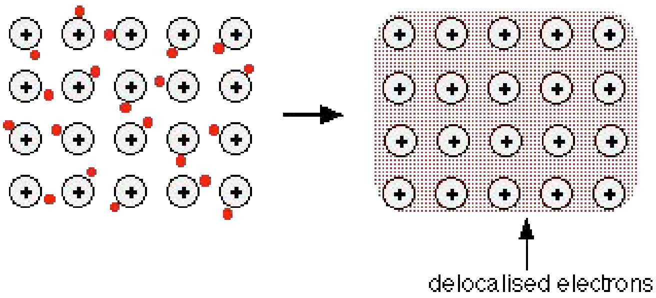
The ionic bond is based on the effective transfer of one or more electrons from the outermost layer of the strong metal to the outermost layer of the strong non-metal; the metal is a potential electron donor, the non-metal, an acceptor.

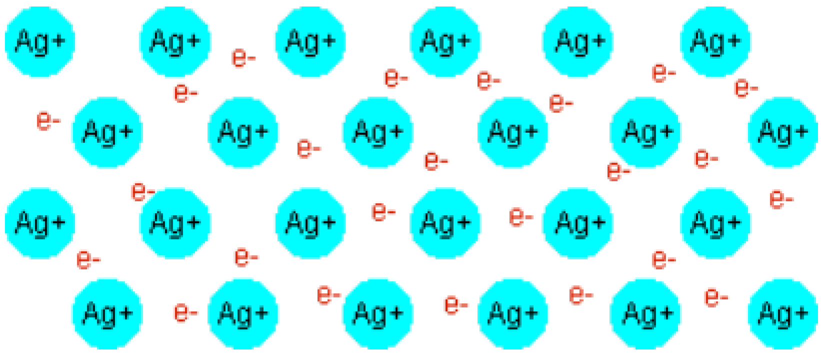
An ionic compound is a combination consisting of a cation and an anion, ions that remain in close proximity to each other, almost in contact, due to Coulombic attraction.

Metallic Bonding:

- Occurs between atoms with low electronegativities and few electrons in their outer shell (1, 2, or 3 electrons).
- Involves the sharing of electrons not between 2 atoms but among an unlimited number of atoms: the phenomenon of electron delocalization throughout the entire sample.
- The metallic atoms, in forming the bond, lose influence over their outer electrons, becoming positive ions whose positions, if the metal is solid, are fixed relative to each other.

Model of metallic bonding:
The outer electrons are delocalized and behave as if they were free, while remaining within the sample.
A metal can be described as an assembly of positive ions surrounded by a weak electronic cloud (or sea) with easily mobile electrons, hence the high electrical conductivity of metals.
- Not directed in space.





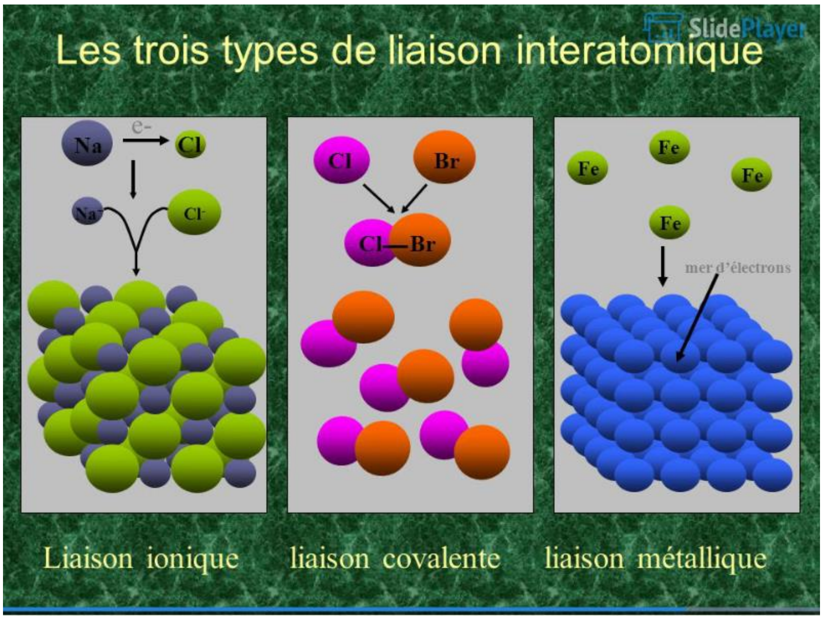
Metals are known for their thermal conductivity, which is very significant. If the metal is heated at a point, the delocalization of electrons allows the transfer of thermal energy through their agitation. This results in the propagation of heat throughout the metal, causing an increase in the temperature of the solid as a whole. Metals are also good electrical conductors. Under the influence of an electric field, even a weak one, a current passes. This is related to the ease with which electrons move within the solid.

Strong Bonds

- Dissociation energy to break strong bonds: 200 to 500 kJ.mol-1

3 types of strong bonds:

- ✓ *Covalent bond:* forms between atoms of similar electronegativities.
- ✓ *Ionic bond:* forms between atoms of very different electronegativities.
- ✓ *Metallic bond:* forms between atoms of similar electronegativities - ensured by a number of electrons less than a pair
- ✓ Much weaker than the other two These are types of limiting bonds: many bonds are intermediate cases between these 3 limiting types.


Les trois types de liaison interatomique
SlidePlayer
Na
e-
Cl
Na+
Cl-
Cl
Br
Cl—Br
Fe
Fe
Fe
Fe
mer d'électrons
Liaison ionique
liaison covalente
liaison métallique