**CHAPTER VIII. Chemical bonds**

**1. Introduction**

 Apart from inert gases (last column of the periodic table), which are monoatomic, all atoms are involved in chemical bonds, forming molecules and/or solids or liquids. In fact, even inert "gases" eventually condense at very low temperatures (or under high pressure). To classify bonds, the two essential notions are bond energies (or their opposites: dissociation energies) and the electronegativities of the atoms bonded. There are two types of bonds, strong bonds (covalent, ionic, and metallic bonds) and weak bonds (hydrogen and Van Der Waals bonds).

**2. the covalent bond: Lewis model**

 Generally speaking, any bond formed by the pooling of electrons is a covalent bond. According to Lewis, electrons belonging to the deeper layers of the atom (core electron) can be ignored, and only the peripheral electrons (valence electrons) of an atom can be involved in bond formation.

**2.1. Lewis representation of atoms**

The Lewis representation shows the external electronic structure or valence layer.

It is represented by :

Dashes - paired electrons or free doublets.

Dots - single electrons.

Empty quantum bin represented by a rectangle.

The valence of an atom :

The number of single electrons gives the atom's valence, i.e. the number of bonds an atom canform.

- Hydrogen has 1 single electron: it is monovalent

- oxygen  has 2 single electrons: it is bivalent.

- Nitrogen  has 3 single electrons: it is trivalent.

- The carbon atom  has 4 single electrons: it is tetravalent.

**2.2. Lewis representation of molecules.**

**- simple bonding covalent :**

Each atom provides an e- from its outer layer to form the bond:



***Example :***





**- Multiple covalent bonding :**

The LEWIS model also allows for the formation of double or triple bonds.

**Example:**



**- Coordinating bond or dative covalent bond :**

One of the two atoms (the donor: A) provides a doublet from its outer layer. The other (the acceptor: B) receives this doublet in the empty square of its outer layer. The dative bond is identical to the covalent bond, but is represented by an arrow from the donor to the acceptor.



The Lewis diagram represents all the binding and non-binding pairs of a molecule (also single e-) but does not indicate the molecule's spatial geometry.



Determining the Lewis scheme is not always easy; for example, for nitrogen, N2, there are three possibilities

 

What is the correct Lewis diagram?

**The octet rule**

 In a molecule or ion, the atoms (2nd and 3rd row of the classification) are associated in such a way that each of them is surrounded by a maximum of one octet of electrons (8e-) (four doublets, binding or non-binding).

**Note:**

There are many exceptions to this rule:

- there are stable molecules in which atoms are surrounded by fewer or more than four pairs of electrons.



**Extension of the octet rule**

From the third period of the classification, up to 6 bonds can be observed around an atom. The presence of 3d atomic orbitals allows these atoms to have more than 8 electrons in the valence shell. The octet rule is no longer satisfied (hypervalent compounds).



**Formal charges**

When a bond is formed, each atom may pool an e-, or one of the two atoms may "contribute" the 2e- to the bond.

During the formation of a bond, there can be a sharing of an e- by each atom or one of the two atoms "contributes" the 2e- of the bond.



In the second case, formal charges appear to indicate that there has been a "loss" of an e- for A and a "gain" of an electron for B.

The sum of the formal charges is equal to the real charge carried by the molecule.

Examples of determining formal charges:

Atom A received two electrons => A2-

Atom B has lost 2 => B2+



Simple approach for constructing the Lewis diagram:

1- Write the electronic structure of each atom.

2-Find the number N of external electrons of each atom. (Valence electrons).

3- Find the number Nl of covalent bonds that the atom must establish to acquire an octet structure Nl = (8 – Ne). (Exception for H, Nl =2-1).

4-Calculate the number Nnl of non-bonding doublets of each atom:

**Nnl = (Ne – Nl)/2**

We can then draw the Lewis representation:

⎫ Place the bonding doublet(s) between the atoms of the molecule (covalent bonds).

⎫ Place the non-bonding doublet(s) around the atoms that have them.

⎫ Check that each of the atoms of the molecule satisfies the octet rule by being surrounded by 4 doublets.

**Examples :**



In this SO2 molecule, experience shows that the bond order is intermediate between a single and a double bond, this molecule exists in the form of a mesomer.



**Mesomerism**

When multiple Lewis formulas can be written for a chemical species and they differ only in the distribution of electrons, then the chemical species is not correctly represented by a single Lewis formula.

Mesomerism then consists of describing the chemical species using all of these Lewis formulas. These formulas are called mesomeric forms or limit forms and have no physical existence. We say that there is resonance between these limiting forms.



**Mesomeric forms**

Insufficiency of the Lewis model

The Lewis model is based on a set of observations and findings, but is not based on any physical laws. This model is incapable:

* interpret in detail the electronic structure of molecules.
* give information on the geometry of molecules

**3. Valence shell electron pair repulsion (V.S.E.P.R.) theory (valence shell electron pair repulsion)**

“Around each atom, the pairs of valence electrons (free or bonding) move as far away from each other as possible in order to minimize their electrical repulsion. » In this theory the molecule is represented by: **AXnEm**

A: central atom.

X: atoms bonded to A and n their number.

E: free pairs on A and m their number.

Knowing that the electronic doublets of the valence layer repel each other, the geometry of the molecule will be that for which the repulsions are minimal, that is, the electronic doublets are as far apart as possible. Thus, in this theory, the geometry of the molecule is determined from the values **​​p =m+n**.

***Examples :***

**p = 3**

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**P = 4**

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**Summary tables:**





**3.1. Application example:**

Let's take the molecules: CO2, N3-, I3-, O3

To determine the geometry of molecules it is necessary:

- determine the number of atoms linked to the central atom

- then determine the formal charge on the central atom and the number of non-bonding doublets (DNL):

Let's try to determine the charge of the central atom in the N3- and O3 molecule

Formal charge = nV – (nDNL+nDL/2)

nV: number of valence electrons of the atom alone

nDNL: number of free pair electrons (DNL) after formation of the molecule

n DL: number of shared bonding electrons

Formal charge on nitrogen (central atom) in the molecule N3- = 5- (0+8/2)=+1

Formal charge on oxygen (central atom) in the O3 molecule = 6- (2+6/2)=+1



**3.2. Modifications des angles valenciels :**

**3.2.1. Influence du nombre n de paires libres.**

Dans la série AX4 ; AX3E1 ; AX2E2, on constate une diminution de l’angle XAX en

passant de n = 0 à n = 2.

CH4 : HCH = 109,5°

NH3 : HNH = 107,3°

H2O : HOH = 104,5°

Cette diminution régulière est due aux répulsions des paires libres qui occupent autour de l’atome A un volume plus important que les paires liées essentiellement bloquées entre A

et X.

**3.2. Modifications of valence angles:**

**3.2.1. Influence of the number n of free pairs.**

In the AX4 series; AX3E1; AX2E2, we see a decrease in the angle

going from n = 0 to n = 2.

CH4: HCH = 109.5°

NH3: HNH = 107.3°

H2O: HOH = 104.5°

This regular decrease is due to the repulsions of the free pairs which occupy a greater volume around atom A than the bound pairs essentially blocked between A and X.

**3.2.2. Influence of the electronegativity of the central atom.**

In the AX3E1 series: NH3, PH3, AsH3; SbH3, we determine experimentally: HNH = 107.3°; HPH = 93.3°; HAsH = 91.8°, HSbH = 91.3°

In the VA group, the electronegativity decreases from nitrogen to antimony, the bonded pairs are more attracted towards the nitrogen atom in NH3 than towards the antimony atom in SbH3, so their repulsion is stronger and the higher valence angle.

**3.2.3. Influence of the electronegativity of X.**

As the electronegativity χ of atom X increases, while A remains the same, bonded pairs are more attracted to X and the valence angle decreases:



The VSPER method quickly provides information on the spatial geometry of molecules, confirmed by X-ray structural analysis.

**4. Dipole moment**

Two charges equal in absolute value but of opposite sign, +q and -q, separated by a distance r, constitute a dipole. It is characterized by a vector of modulus equal to the product q×r, oriented, by convention, from negative to positive charge (from - to +).

For example, in a polar diatomic molecule, each atom carries a partial charge δ or -δ, where 0 < δ <|Qe|: 

The dipole moment is then a vector pointing towards the least electronegative atom:

Let q be the positive charge. If d is the distance between the two barycenters, the electric dipole moment is a vector whose modulus is, by definition :

**μ.= q·d**

The unit is the Coulomb. Meter (C.m) .but debye is usually used, based on the old unit of charge ues (meaning "electrostatic unit") :

1 debye (D) = 10−18 ues·cm = 3, 3 ×10−30 C·m.

**1 D = 3.33564×10-30 C.m**

**Examples**

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The H2O molecule. The two arrows along the bonds are the two components of the electric dipole moment.

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 Components of the dipole moment of BF3 and CF4 molecules.

|  |  |
| --- | --- |
|  composé  | μ (D) |
| H2O | 1.855 |
| H2S | 0.978 |
| NH3 | 1.472 |

|  |  |
| --- | --- |
|  composé  | μ (D) |
| HF | 1.826 |
| HCl | 1.109 |
| HBr | 0.827 |
| HI | 0.448 |
|  |  |

**5. Chemical bonding in the quantum model :**

**5.1- Molecular orbital theory (LCAO method):**

This method, called Linear Combination of Atomic Orbitals (LCOA), proposed by Mulliken in 1932, consists in admitting for a diatomic molecule that the molecular orbital 𝜓, the wave function describing the (e) of the bond in molecule AB, can be presented as a linear combination of the two atomic wave functions 𝜓RA and 𝜓RB shared by the two atoms A and B. Thus, when a bond is formed between atoms A and B, the two atomic orbitals (A.O.) merge (overlap) into molecular orbitals (M.O.). According to this method, M.O.s have the form of a linear combination of atomic orbitals 𝜓Ri.

.𝜓=Σ𝐶𝑖 𝜓𝑖𝑖 In the case of a molecule: A-B 𝜓= 𝐶𝐴𝜓𝐴+𝐶𝐵𝜓𝐵

The combination of N atomic orbitals gives N molecular orbitals, half of which (N/2) are binding MOs: linear combinations of MOs of the same sign in the overlap region, i.e. positive overlap.

The remaining N/2 of M.O.s are antibinding, i.e. M.O.s relative to A.O.s of opposite sign, i.e. negative overlap. Antiliant M.Os are represented by a star \*.

Note:

An orbital is a volume in space where the probability of finding an electron is 95%.

a- Formation and nature of bonds :

- axial overlap: σ bond

This is an overlap of two s-orbitals, or of an s-orbital and a p-orbital, or of two coaxial p-orbitals. The M.Os thus formed are called 𝜎-orbitals; the axial overlap gives rise to two sigma M.Os (σ, σ\*); there is free rotation around the σ-bond.

 

 Axial overlap : formation of the σ bond

**- Lateral overlap: π-bonding**

This concerns p orbitals whose axes are parallel, and this overlap leads to a π orbital. The corresponding bonds are weaker than σ bonds, and in the absence of axial symmetry of the M.O.s, π bonds do not allow rotation around the π bond.



 Lateral overlap π-bond formation

**b- Energy aspect**

When atoms A and B are far apart (i.e. not interacting), their energy is zero. By convention, the atoms are said to be at infinity to each other. On the other hand, when atoms A and B are close to each other, they enter into interaction. The interaction energy at that moment is equal to the sum of :

- energy of attraction: nucleus of A (or B) with electrons of atom A (or B)

- energy of repulsion: nucleus A-core B and electrons A-electron B

 **Énergie du système constitué de deux atomes A et B en fonction de la distance d’ internucléaire**

En effet les courbes de variation de l’énergie des orbitales d’un système formé par deux atomes en fonction de leur distance, confirment ainsi le caractère liant ou antiliant des deux O.M.

Si le doublet d’é commun entre les deux atomes A et B de la liaison A-B occupe l’orbitale moléculaire liante ou O.M : σ la molécule est plus stable c’est le cas de la courbe (X), par contre la courbe Y correspond à l’énergie de l’orbitale moléculaire σ\*, plus les deux atomes sont proches plus l’énergie est grande, mais elle n’existe pas de position d’équilibre stable, la molécule serait moins stable que les deux atomes séparés.

**Exemple :**

Molécule de H2

