The chemical bond

Introduction

How is the H_2 molecule formed ? Does the H_3 molecule exist ?

Why doesn’t the He_2 molecule exist ?

The notion of molecule is one of the fundamental concepts of chemistry. A molecule is a group of atoms preserved during changes in physical state.

To answer the previous questions, it is necessary to have a good understanding of the concept of chemical bond and the rules imposed by Lewis' theory which is essentially based on the topology of the molecule.

I/ The chemical bond

The chemical bond is a lasting interaction between two atoms, ions or molecules at a distance allowing the stabilization of the system and the formation of a chemical substance.

This notion includes a diversity of phenomena shaping matter. Thus, the chemical bond can be covalent, ionic, metallic, van der walls, hydrogen,etc.

1/ Definition

A chemical bond is the sharing of two electrons between two atoms in a molecule.

2/ The localized connection

The chemical bond can be localized: this is the case where the distance between the center of the electronic cloud which ensures the link between the two atoms and their nuclei is constant, just as it can be delocalized.

Example :

1/ In the hydrogen chloride HCl molecule the electronic cloud between chlorine and hydrogen is always located in part of the fixed space between the two atoms (**figure 1**).

2/ In the benzene molecule C_6H_6 the electron density between the carbon numbered 1 and the carbon numbered 2 is not constant over time(**figure 2**).

$H - Cl$

Fig1: Localized connection

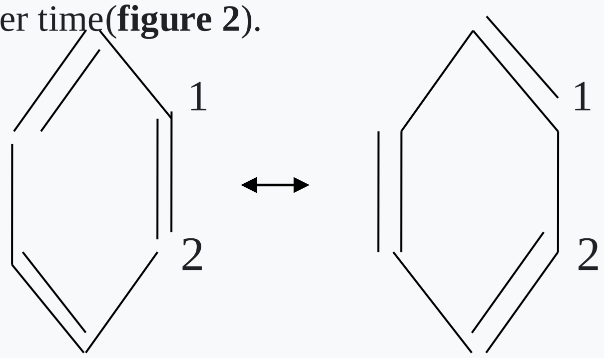


Fig2: Delocalized connection

Noticed:

It should be noted that our study will mainly focus on localized connections.

Depending on the energy required to break a bond, the latter can be classified as strong bond or weak bond.

3/ The strong bond and the weak bond

Weak bonds are explained by polarities between molecules while strong bonds are described by a sharing or transfer of electrons between atoms.

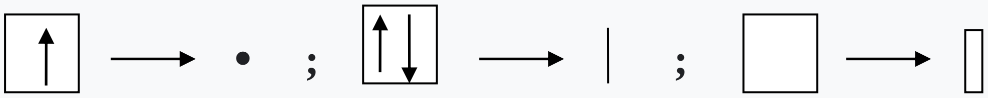
Ionic, covalent and metallic bonds are strong bonds, but weak bonds are mainly represented by Van Der Walls bonds and hydrogen bonds.

II/ Representation of chemical bonds

1/ Lewis representation

The Lewis diagram is a two-dimensional representation of the electronic structure of the atoms making up molecules.

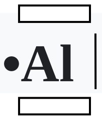
In this representation, an electron is indicated by a dot and an electron doublet by a line.

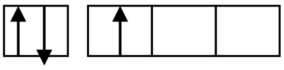


Example :

$$_{13}Al: 1S^2\ 2S^2\ 2P^6\ \underbrace{\mathbf{3S^2 3P^1}}_{\text{External layer}}$$

$_{13}Al$: $_{10}$[Ne] $\mathbf{3S^2}$ $\mathbf{3P^1}$





2/ construction of Lewis molecular diagram

To establish the Lewis molecular diagram, we must follow the steps:

***** Represent the valence electrons of each atom in quantum boxes then in the form of a Lewis atomic diagram.

***** Identify the central atom:

- it is generally the one which represents the center of the molecule.
- If we cannot identify it, we will take the one which has the greatest number of single electrons.
- If two atoms have the same number of valence electrons, the central atom will be the least electronegative.

* Assign the charge that the molecule carries, in the case of compound ions, to the most electropositive atom if the charge is positive, if it is negative it will be attributed to the most electronegative atom.

* Exploit all or the maximum of the valence electrons of the central atom to establish bonds with the lateral atoms.

* Construct the Lewis diagram with the various bonds uniting the central atom to the other atoms.

* Count the electrons belonging to the central atom and those to the side atoms to verify the byte rule.

3/ Byte rule

In a compound, charged or neutral, each atom engaged in a bond seeks to acquire the electronic configuration of the rare gas that is closest to it in the periodic table.

Example :

Representation of the Lewis diagram of molecules:

$H_2PO_4^-$; $H3O^+$; $HClO_4$

III/ The different types of chemical bonds

Chemical bonds are only a manifestation of attractive interactions between atoms, the origin of which is either electrostatic (ionic bond, hydrogen bond), or purely quantum (covalent and metallic bonds, bondsVan der Waals/London type). In this paragraph, we present the different types of bonds and their signatures at the level of atomic structure.

1/ The covalent bond

It is the sharing of two electrons between two atoms that are identical or having diferent electronegativities.

$$A\bullet + \bullet B \longrightarrow A \bullet\bullet B \qquad \text{or} \qquad A - B$$

Example :

Representation of the Lewis diagram of molecules and type of bonds between atoms:

H_2, Cl_2, H_2O, BH_3.

H_2 : $_1H : 1S^1$ $H\bullet$

$H\bullet + \bullet H \longrightarrow H{\bullet\bullet}H$ or $H — H$

Cl_2 : $_{17}Cl : 1S^2 2S^2 2P^6 \mathbf{3S^2 3P^5}$

$_{10}[Ne]\ \mathbf{3S^2 3P^5}$ $|\overline{\underline{Cl}}\bullet$

$$|\overline{\underline{Cl}}\bullet + |\overline{\underline{Cl}}\bullet \longrightarrow |\overline{\underline{Cl}}\bullet\bullet\overline{\underline{Cl}}| \equiv |\overline{\underline{Cl}}—\overline{\underline{Cl}}|$$

H_2O : molecule constituted of 2elements H and O.

$_1H$: $H\bullet$

$_8O : 1S^2 \mathbf{2S^2 2P^4}$

$_2[He]\ \mathbf{2S^2 2P^2}$ $\bullet\overline{\underline{O}}\bullet$

$$2\,H\bullet + \bullet\overline{\underline{O}}\bullet \longrightarrow H\bullet\ \bullet\overline{\underline{O}}\bullet\ \bullet H \equiv H—\overline{\underline{O}}—H$$

Noticed:

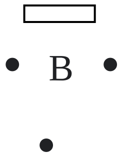
In reality the H2O molecule is not linear, it is bent and the HOH angle is 107°28'.

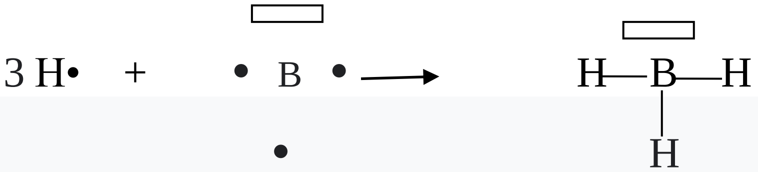
BH_3 : molecule constituted of 2elements B and H.

$_1H$: $H\bullet$

$_5B : {}_2[He]\ \mathbf{2S^2 2P^1}$

$_5B^* : {}_2[He]\ \mathbf{2S^1 2P^2}$





2/ The polarized covalent bond

When two bonded atoms A and B have different electronegativities, we observe a movement of the electronic cloud from the least electronegative atom B , towards the most electronegative atom A.There is the appearance of partial charges on the two atoms $+\delta$ and $-\delta$.

In this case the bond is polarized covalent and we note: $^{-\delta}A - B^{+\delta}$

Example :

In the H Cl molecule, the bond between the two atoms H and Cl is polarized covalent.

Notation: $^{+\delta}H{-}Cl^{-\delta}$ (chlorine atom is more electronegative than hydrogen).

3/ The ionic bond

When the difference in electronegativities of the bonded atoms A and B takes a maximum value, we observe a total relaxation of the electron cloud towards the most electronegative atom, assumed A. There is charge partitioning on the two atoms -1 and +1 .

In this case **we note**: $^{-}A{-}B^{+}$

Example :

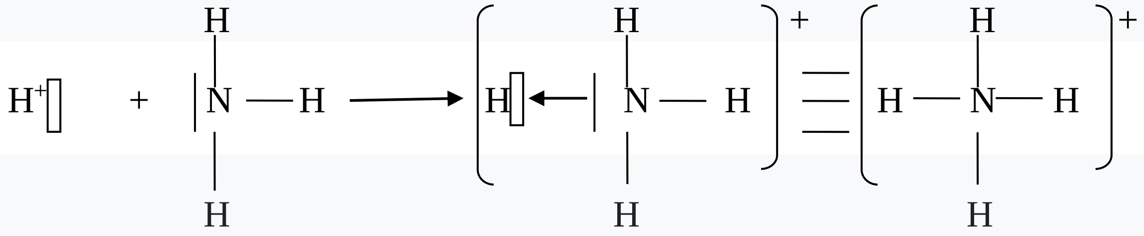
In the sodium chloride molecule NaCl, the bond between the two atoms Na and Cl is ionic.

Notation: $Na^{+}{-}Cl^{-}$ (the chlorine atom allows to VII_A group and the sodium to I_A).

4/ The dative connection

It is the sharing of an electronic doublet between an atom B which has a non-bonding doublet and an atom A which has a vacant cell.

Example: The NH_4^+ charged molecule



IV/ Ionic character of a polarized covalent bond.

1/ Concept of the dipole moment

In a polarized covalent bond between two atoms A and B there is a movement of the electronic cloud towards the most electronegative atom and consequently partition of two charge poles $+\delta$ and $-\delta$, hence the presence of a dipole moment noted μ_{AB} directed from the positive charge to the negative charge.

$$\|\vec{\mu}_{AB}\| = \mu_{AB} = |\text{charge}| \times \text{distance} = |q| \times d = |\delta.e| \times d$$

Unit of dipole moment:

In the IS(MKSA) system μ_{AB} is expressed in coulombs. Meter (C.m).

μ_{AB} can also be expressed in Debye (D) ($1D = 3{,}33.10^{-30}$ C.m)

2/ Percentage of the ionic character

Each polarized covalent bond is associated with a value corresponding to the percentage of the ionic character.

The polarized covalent bond $^{-\delta}A - B^{+\delta}$ is linked to δ.

- If $\delta = 0$ The bond is pure covalent.

- If $\delta = 1$ The bond is pure ionic.

% ionic character = (real μ / theoretical μ) × 100

V/ Geometry of molecules: VSEPR theory (Gillespie rule)

The VSEPR (valence shell electron pair repulsion) theory is designed by Ronald Gillespie around the 1950 to predict the geometries of small molecules.

This method is essentially based on the repulsions of electrons from electronic pairs in the valence shell.

1/ Principle of the VSEPR theory

The principle of the method resulting from this theory is based on the fact that the pairs of electrons made up of non-bonding doublets of the valence shell of the central atom of a polyelectronic building repel each other (same negative charge) and each other. move as far apart as possible to minimize the energy and increase the stability of the chemical system in question, which will allow the molecule to acquire a geometry in space according to the nature of the atoms constituting the chemical structure.

2/ Limit boundary of the VSEPR theory

This theory only applies to molecules or compound ions, of the form AXmEn.

A : represents the central atom , X : atom(s) bonded to A , E: free doublets .

m: number of atom(s) X bonded to A , n: number of free doublet(s) around A .

Example :

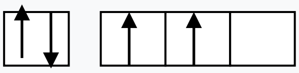
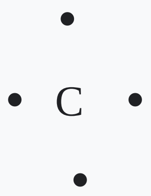
a/ Represent the following molecules according to the Lewis model:

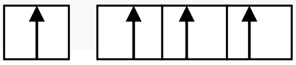
CO_2 , H_2O.

b/ What geometry does each molecule correspond to, according to the Gillespie model.

Correction :

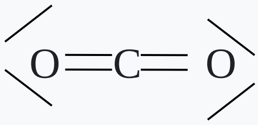
CO_2 :

$_6$C : $_2$[He] **$2S^2 2P^2$**  (exitation state : )

$_6$C* : $_2$[He] **$2S^1 2P^3$** 

$_8O$: $_2$[He] $\mathbf{2S^2 2P^4}$

CO_2 :



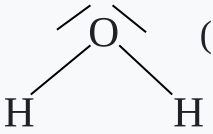
(C central atom ; O lateral atom)

H_2O :

$_1H$: H•

$_8O$:

H2O :



(O central atom ; H lateral atom)

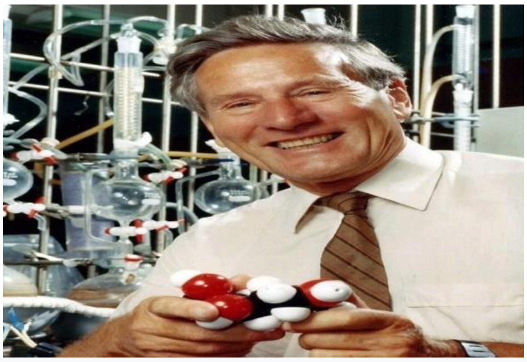
b/ Molecular geometry

- The CO_2 molecule is of the form AX2 (A=C, X=O, m=2 and n=0), then: m+n=2+0=2

Linear structure.

- The H_2O molecule is of the form AX2E2 (A=O, X=H, m=2 and n=2), then: m+n=2+2=4

Bent or V-shaped structure.

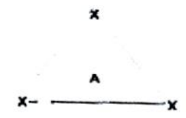
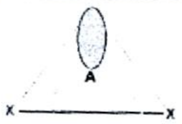
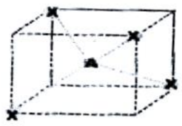
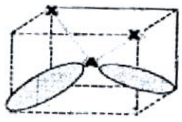
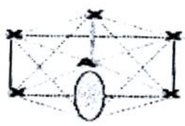
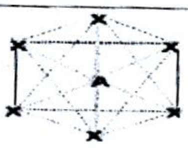


Annex 1

Ronald J. Gillespie, C. M., born August 21, 1924 in London and died February 26, 2021, professor of chemistry at McMaster University in Canada, is a specialist in the field of molecular geometry. He was appointed a Member of the Order of Canada on June 29, 2007. He was educated at the University of London, where he received a BSc in 1945, a Doctorate (Ph.D.) in 1949 and a Doctorate (D.Sc.) in 1957. He was a lecturer at University College London, England from 1950 to 1958. In 1958 he moved to McMaster University in Hamilton, Ontario (Canada), where he became a full professor in 1960. He finished his career as professor emeritus. He was made a Fellow of the Royal Society of Canada in 1965. Ronald Gillespie worked on the VSEPR model of molecular geometry, which he developed himself with Professor Ronald Nyholm. He wrote several books on this theory. He also worked on the interpretation of the covalence radius of the fluorine atom. For most atoms, the covalence radius is half the length of a single bond between two identical atoms in a neutral molecule. The calculation is more difficult in the case of fluorine because of its high electronegativity and its small atomic radius. Gillespie made a theoretical assessment of this covalence radius using an examination of the bond lengths between fluorine and several other atoms.

Annex 2

Prévision de la géométrie des molécules selon la méthode VSEPR (Règle de Gillespie)

Géométrie de la molécule Globale *AXmEn*	*(m)* *Nombre d'atomes X lies à A*	*(n)* *Nombre de doublets libres autour de A*	*(m+n)*	**Type d'hybridation**	**Représentation géométrie propre de la molécule**	**Exemple**
AX_2	2	0	2	Sp	X ------ A ------ X	Linéaire CO_2–C_2H_2
AX_3	3	0	3	Sp^2		Triangle Equilatéral C_2H_4, BCl_3
AX_2E	2	1	3	Sp^2		Triangle en (V) inversé SO_2, $SnCl_2$
AX_4	4	0	4	Sp^3		Tétraèdre CH_4, $SiCl_4$, NH_4^+
AX_3E	3	1	4	Sp^3		Pyramide Trigonale NH_3, NF_3, PF_3
AX_2E_2	2	2	4	Sp^3		Forme en (V) inversé H_2O, H_2S
AX_5	5	0	5	Sp^3d		Pyramide base carrée PCl_5
AX_6	6	0	6	Sp^3d^2		Bipyramide base carrée SF_6