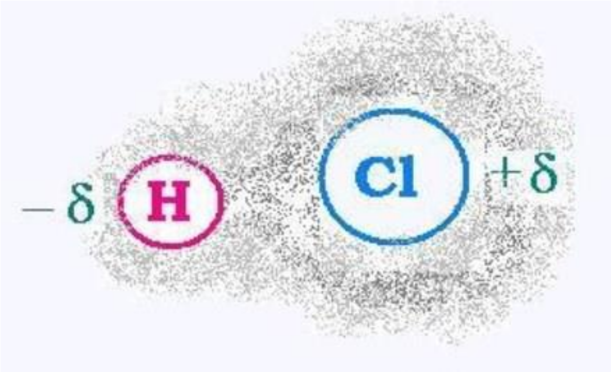
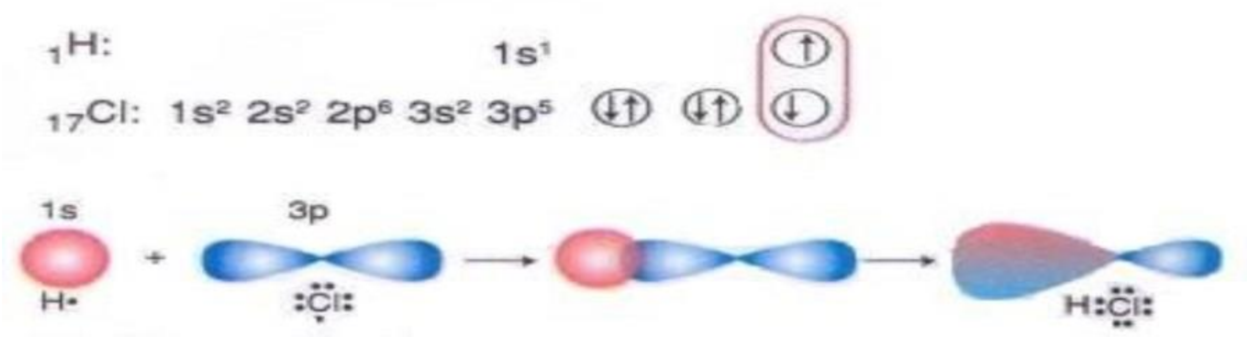
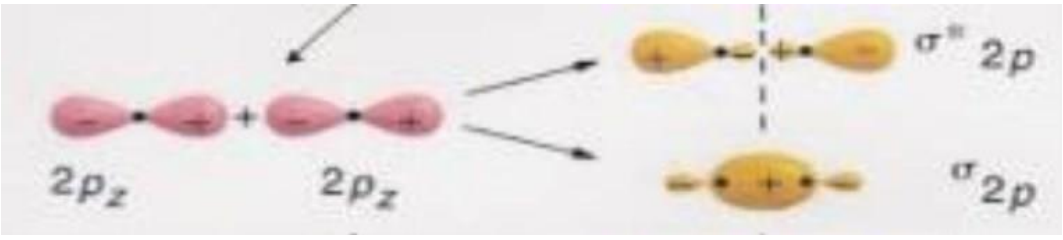
Example : HCl



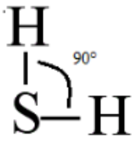


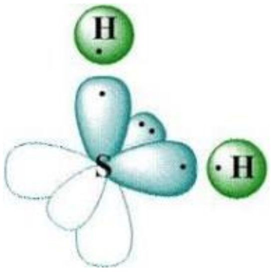


Example: H_2S

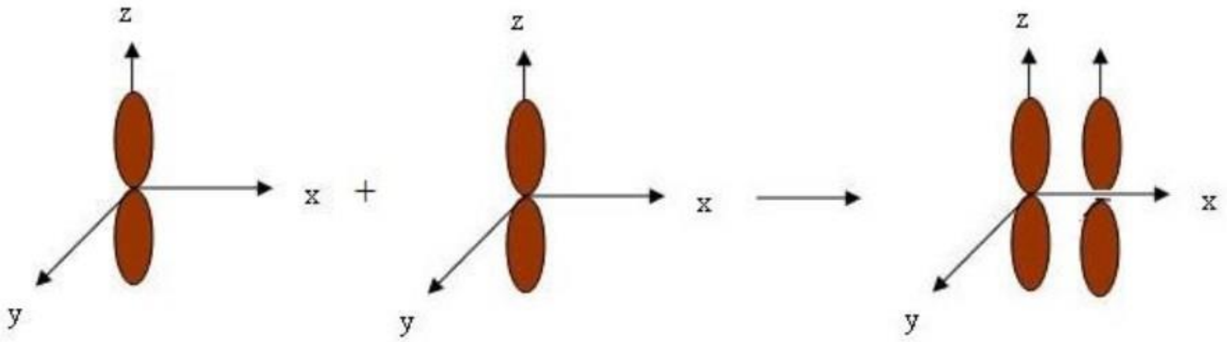
$_1H$ $_1s^1$

$_{16}S$ $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^4$

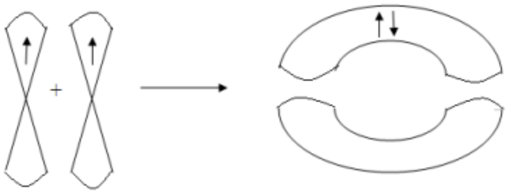


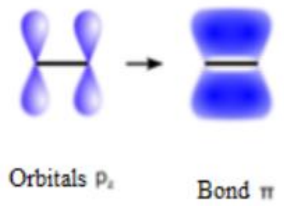


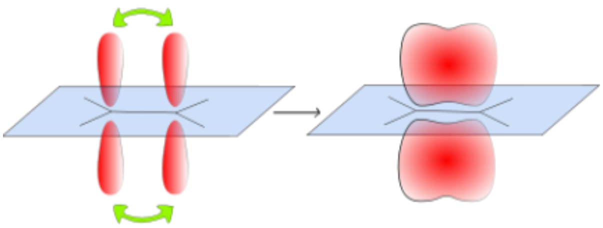
⟹ ***Lateral overlap:*** results from an interaction between electrons in parallel p orbitals. This overlap gives rise to a π bond.

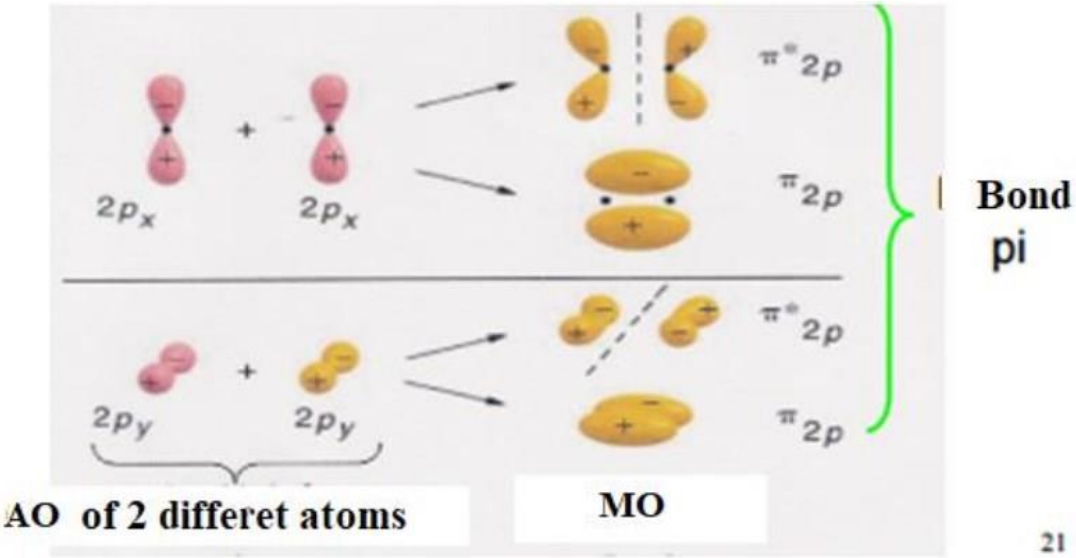


The π bond :









To better understand the overlapping mode, we use the representation or Lewis diagram before and after bonding.

II- LEWIS diagram:

▶For atoms, we represent the electrons of the outermost shell (unpaired electrons or lone pairs).

$_1$H : 1s^1 H•

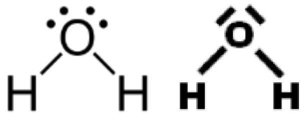
$_7$N : 1s^2 2s^2 2p^3 N

$_8$O : 1s^2 2s^2 2p^4 O

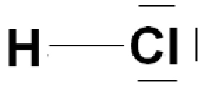
$_{17}$Cl : 1s^2 2s^2 2p^{6}3s^2 3p^5 C

▶For molecules, we represent the electrons in bonds (bonding pairs) and the lone pairs.

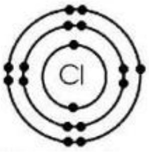
H_2O :

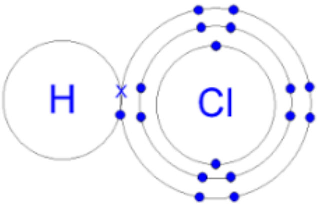


HCl:

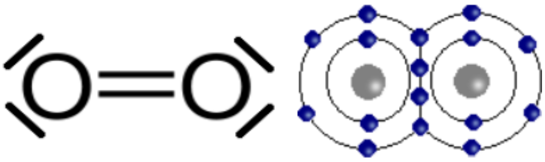


$_{17}$Cl 1s^2 2s^2 2p^6 3s^2 3p^5

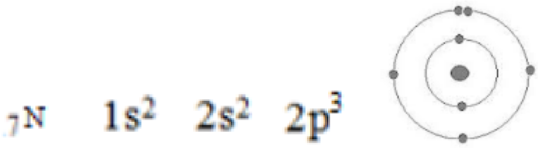




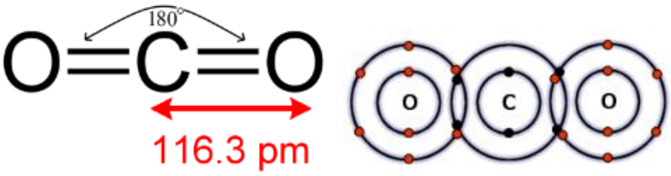
O_2:



N_2:



CO_2:



III- Types of bonding.

In chemical bonding, molecular orbitals are formed from atomic orbitals. There are several types of bonding.

III-1- Covalent bond :

A covalent bond involves the sharing of two unpaired electrons belonging to separate orbitals to achieve the nearest noble gas configuration (saturated valence shell). Covalent bonds can be single (σ) bonds, double bonds (π), or triple bonds (π').

Generally, the σ bond is more energetic. Covalent bonds can occur between monoatomic or polyatomic atoms:

Example :

H-H, Cl-Cl, O=O Homonuclear diatomic molecules.

H-Cl, S=O Heteronuclear diatomic molecules.

H_2O, CH_3COOH H_2SO_4 Polyatomic molecules.

III-2- Ionic bond :

Ionic bonding involves the transfer of electrons between an electropositive atom and an electronegative atom. Typically, this occurs between atoms in the first and second column of the periodic table with elements in the 17th column. If A and B in a molecule AB have different electronegativities, one atom easily attracts the electrons from the other, resulting in the formation of A+ and B- ions.

$A\text{-}B \longrightarrow A^{+}, B^{-}$

So, there is a transfer of electrons from one to the other.

Example :

Na et $Cl \longrightarrow Na^{+}, Cl^{-}$

Na et $Br \longrightarrow Na^{+}, Br^{-}$

Mg et $2Cl \longrightarrow Mg^{2+}, 2Cl^{-}$

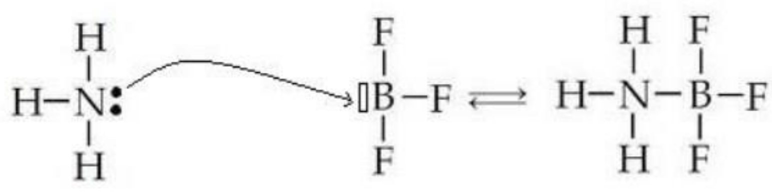
K et $Cl \longrightarrow K^{+}, Cl^{-}$

Ionic bonding is not rigid.

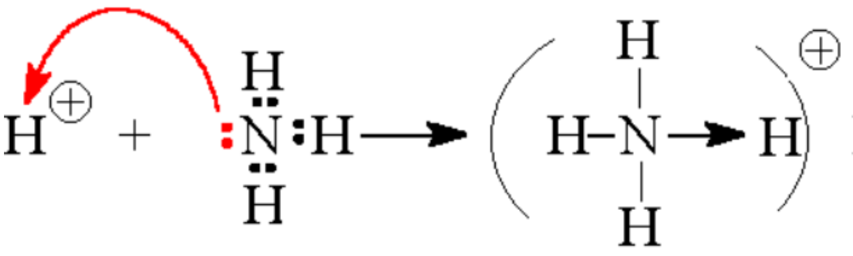
III-3- Dative or Coordinate bonds:

Dative bonds are formed between an atom with a "lone" pair (electron donor) and another atom with an empty orbital (electron acceptor). The lone pair is donated to the empty orbital.

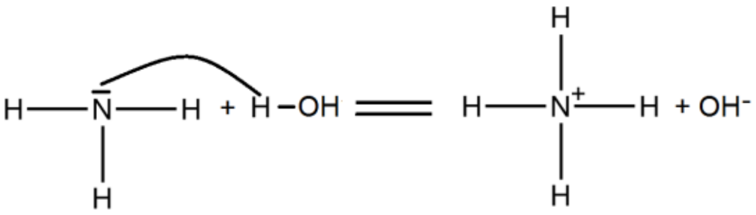
Example: NH_3+BF_3



NH_3+H^+

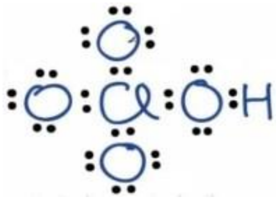


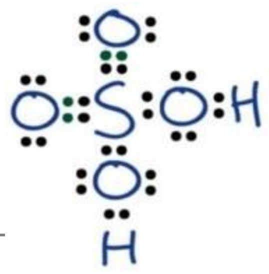
Formation of Ammonium Ion.



$HClO_2$ $HClO_3$

$HClO_4$ H_2SO_4





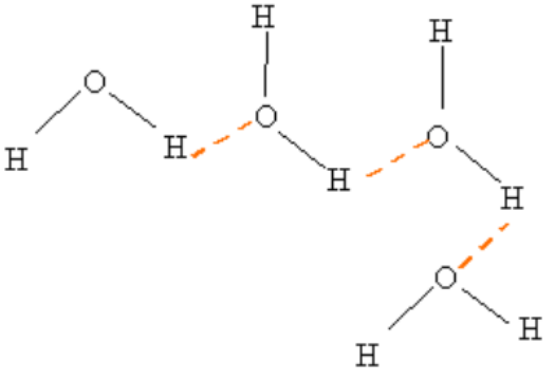
SO_2

III-4- Hydrogen Bonding:

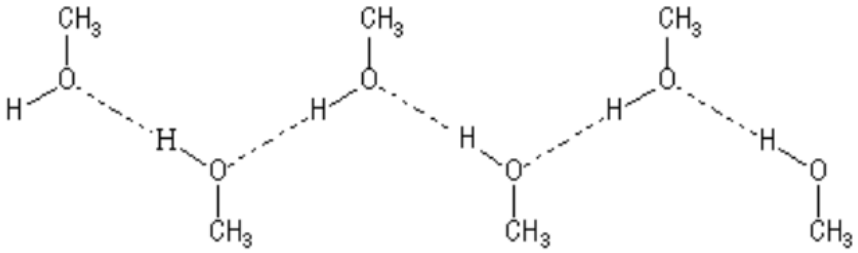
Hydrogen bonding occurs between an atom with a lone pair of electrons and an electronegative atom. It is an electrostatic type of chemical bond.

There are two types of hydrogen bonds:

Intermolecular Hydrogen Bonding: (between two molecules



Intramolecular Hydrogen Bonding: (within the same molecule)



IV- Dipôle Moment :

The dipole moment arises from the difference in electronegativity between two atoms in a bond, leading to the displacement of electrons from the electropositive atom to the electronegative atom through the σ bond. This electron displacement creates a dipole (the electron density is heterogeneous across the bond, inducing a dipole moment).

The dipole moment (μ) is defined as the product of the charge (Q) and the distance (d) that separates the centers of positive and negative charges.

Mathematically, $\mu = Q \times d$.

The dipole moment is a vector directed from the center of the negative charge to the center of the positive charge.

$A^{+}\delta \underline{\qquad r \qquad} B^{-}\delta$

$\vec{u}$ $\|\vec{\mu}\| = \boldsymbol{\delta}.\ \mathbf{r}$

$\|\vec{\mu}\| = \underbrace{|\delta|}_{\text{Displaced Charge}} \text{ x } \underbrace{d}_{\text{distance in meters}}$ (c. m: Coulomb. Meter).

Another unit for dipole moment is: Debye

The Debye =>1D = 3,7 10^{-30} C. m = 10^{-18} C.G.S.

MKSA : e^{-}= 1,6x10^{-19} C = 4,8x10^{-10} u C.G.S

1Amgstrun :1A° = 10^{-10}m

A molecule with a non-zero dipole moment is said to be polar. This means it has an asymmetric distribution of charges.

Polar molecules interact with each other and with molecules of other substances via dipole-dipole forces.

Note :

The dipole moment is zero in the following cases :

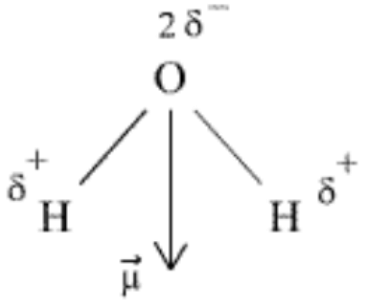
- In a homonuclear diatomic molecule: H_2, Cl_2, N_2 => $\vec{\mu} = 0$
- In a symmetric linear molecule: O=C=O => $\vec{\mu}_{CO2} = 0$.

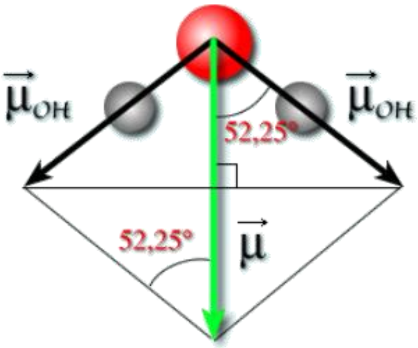
In the case of a triatomic or polyatomic molecule (containing 2 or more bonds), the resulting dipole moment is calculated.

To calculate the dipole moment of a molecule, it is essential to know the partial charge values on each atom and the distance between them. The total dipole moment can be obtained by vectorially summing the individual bond dipole moments.

Example:

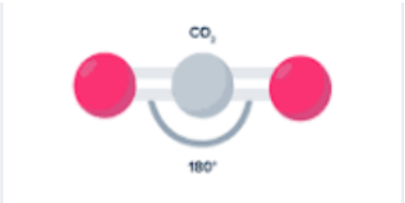
Water (H_2O): The water molecule has a bent shape, and the difference in electronegativity between oxygen and hydrogen creates an uneven distribution of charges, resulting in a dipole moment.

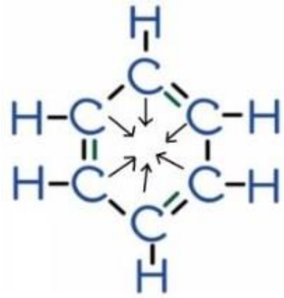




$$\vec{u}_T = \sqrt{u_1^2 + u_2^2 + 2u_1u_2\cos\theta}$$

Carbon Dioxide (CO_2): Although the C=O bonds are polar, the molecule is linear, and the dipole moments of the bonds cancel each other out, making the molecule non-polar.





$\overrightarrow{U_T} = 0$

The ionic character:

The ionic character (I) measures the degree of ionic nature in a bond and is determined by the equation:

$$I = \frac{U_{experimental}}{U_{theoritical}} 100\%$$

$U_{th}e_{\ oritical} = |e| \times d$ ($|e| = 1{,}6\ 10^{-19}$, d: distance)

$U_{experimental} = |\delta| \times d$ ($|\delta|$: actual charge)

So: $I = \frac{|\delta| \times d}{|e| \times d} 100\%$ $(\delta << e)$

Certainly, ionic bond: $i = 100\%$

Certainly, covalent bond: $i = 0\%$

65% ionic character and 35% covalent character: $i = 65\%$

If the bond were purely ionic (100%), the charge (δ) would be equal to e. In this case, we refer to the electric dipole moment $\mu_e = \mu_{the} = e.r$.

Molecule	r (A°)	$\mu_{theo} = e.\ r$	$\mu_{exp} = \delta.\ r$	$\frac{\mu exp}{\mu theo}$x100
HF	0,92	4,42	1,91	45
HCl	1,27	6,09	1,07	17,5
HBr	1,41	6,77	0,79	12
HI	1,61	7,79	0,38	5

The dipole moment influences the physical and chemical properties of substances, such as their boiling point, solubility, and intermolecular interactions

V- Atomic orbital hybridisation:

Hybridisation involves mixing atomic orbitals of the outer shell. This phenomenon can occur after electron excitation.

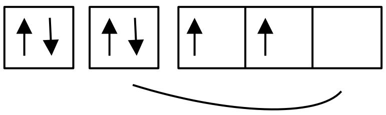
There are three types of hybridisations: sp^3, sp^2, sp.

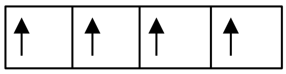
V-1- Sp^3 hybridisation:

It involves a combination of 3 p orbitals and 1 s orbital, resulting in 4 equivalent sp^3 hybridised orbitals.

Carbon Atom:

${}_6C$: $1s^2\ 2s^2\ 2p^2$





Excitation of e^-

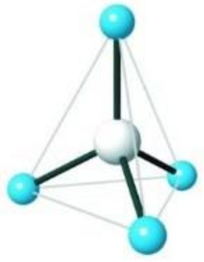
4 orbitals hybridised sp^3

$1\ OA_s + \quad 3\ OA_p \longrightarrow 4OA_{\text{hybridised}}\ sp^3$

Carbon hybridised sp^3 { 4 σ bonds.

Tetrahedral molecular geometry.

Bond angles are around 109° 27'.



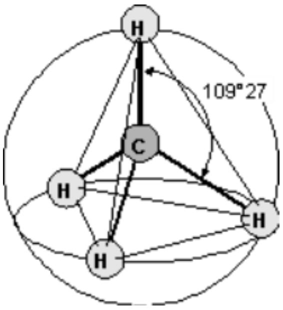
It is a mixture of atomic orbitals from the same shell to form new hybrid orbitals.

sp^3 hybridization occurs when one s orbital and three p orbitals mix to form four equivalent sp^3 hybrid orbitals. The four hybrid orbitals participate in the formation of sigma bonds, which are single covalent bonds.

This type of hybridization is observed when a central atom forms four sigma bonds, usually resulting in a tetrahedral geometry.

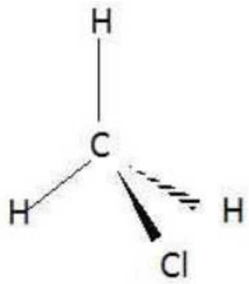
The sp^3 hybrid orbitals arrange themselves in a tetrahedral geometry around the central atom to minimize electronic repulsion, with bond angles of approximately 109.5 degrees.

Example : CH_4 Molecule:

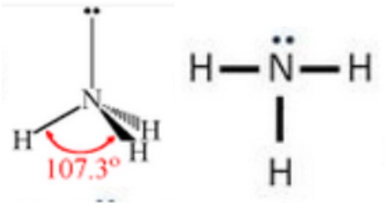


In the methane (CH_4) molecule, the carbon atom has four sp^3 hybrid orbitals, each forming a sigma bond with a hydrogen atom.

Example : CH_3Cl Molecule



Example : NH_3 Molecule:



V-2- Sp^2 hybridisation :

It involves a combination of one s orbital and two p orbitals, resulting in three equivalent sp2 hybridized orbitals and one pure p orbital.

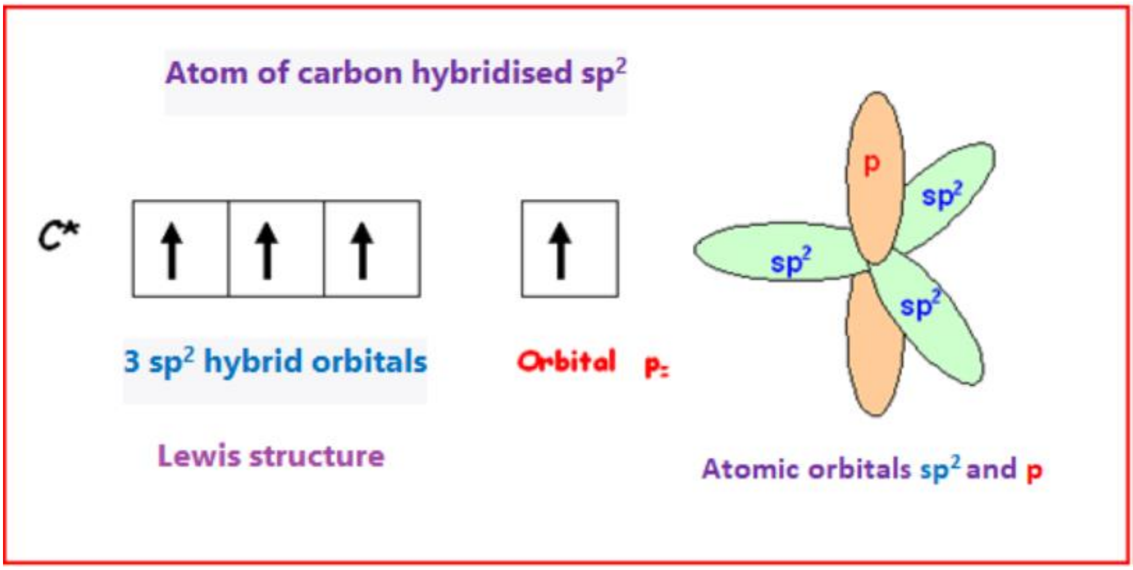
sp^2 hybridization occurs when one s orbital and two p orbitals mix to form three equivalent sp^2 hybrid orbitals.

The sp^2 orbitals arrange themselves in a trigonal planar geometry around the central atom.

The bond angles are approximately 120 degrees to minimize electron repulsion.

In sp^2 hybridization, three sp^2 hybrid orbitals form sigma bonds.

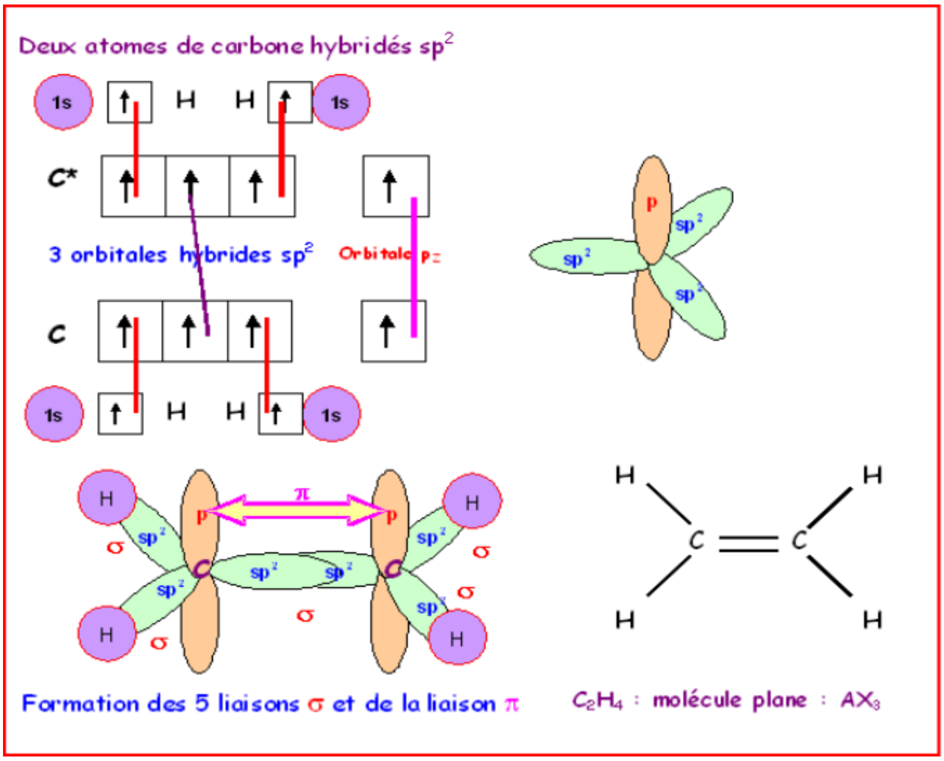
The unhybridized p orbital participates in the formation of pi bonds.



Hybridised sp^2 Carbon:3 σ bonds and 1 π bond.

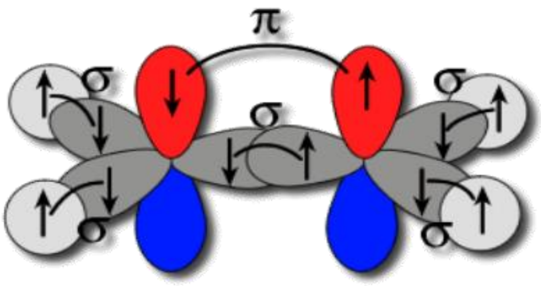
Trigonal molecular geometry (planar triangle).

Bond angles are approximately 120°



Example: C_2H_4: The molecule of ethylene, sp2 hybridisation, trigonal shape.

Ethylene (C_2H_4): Each carbon atom in ethylene is sp^2 hybridized. The two carbon atoms form a sigma bond by sharing an sp^2 orbital, and each carbon forms two other sigma bonds with hydrogen atoms. The unhybridized p orbitals on each carbon form a pi bond, creating a double bond between the carbons.



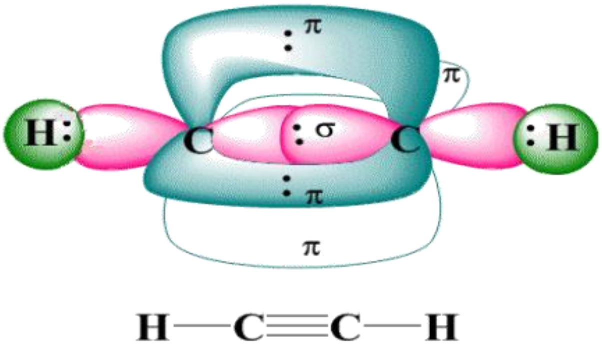
V-3- Sp hybridisation:

Hybridization sp results from the mixing of one s orbital and one p orbital of the same atom, which have the same shape and energy. This process gives rise to covalent bonds with a linear geometry, with a 180° angle between them. During sp hybridization, one 2s orbital combines with one 2p orbital to form two sp hybrid orbitals. The remaining two 2p orbitals remain unchanged and are perpendicular to the sp orbitals.

It involves a combination of one s orbital and one p orbital, resulting in two equivalent sp hybridised orbitals and two pure p orbitals.

Example : C_2H_2 molecule:

In ethyne, each carbon atom uses sp hybridization to form two sp hybrid orbitals. One of these orbitals forms a σ bond with the other carbon atom, while the other forms a σ bond with a hydrogen atom. The non-hybridized p orbitals form two π bonds, one on each side of the carbon-carbon σ bond, thus creating a triple bond.



Hybridised sp Carbon: 2 σ bonds and 2 π bonds.

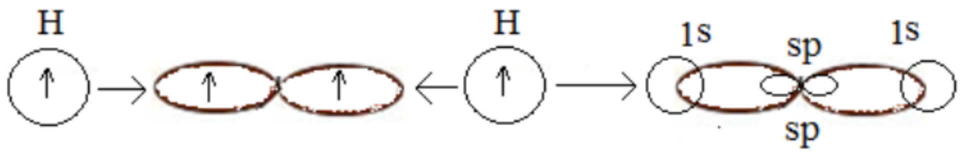
Linear geometric shape.

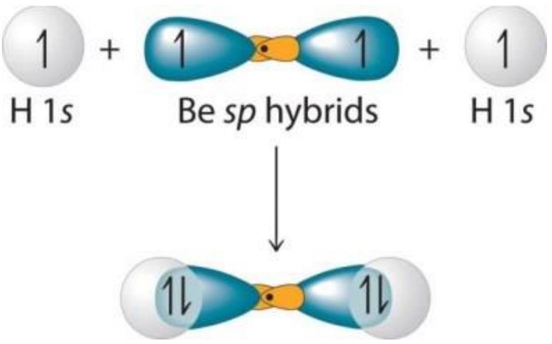
The angles are approximately 180°.

Example: BeH_2: sp hybridisation, linear shape.

$_4Be$ $\{$ $1s^2$ $2s^2$ Ground state.

$2s^1$ $2p^1$ Valence state.





VI-Diagram of diatomic molecular orbitals:

The interaction between two atomic orbitals leads to two molecular orbitals with different characteristics.

► One of these molecular orbitals is more stable than the more stable of the two atomic orbitals; it is called a ***bonding molecular orbital.***

► The other molecular orbital is less stable than the less stable of the two atomic orbitals; it is called an ***antibonding molecular orbital.***

In the energy diagram, two cases can be distinguished :

For homonuclear diatomic molecules of type A_2 : **Cl_2, O_2,N_2**, the energy level is the same.

For heteronuclear diatomic molecules of type A-B : HCl, CO, NO, different energy levels exist, with the more electronegative element placed to the right and at the bottom of the diagram.

-If $\Sigma e^- \leq 14$ so the $\pi(x,y)^L$ orbital is placed before the σz^L orbital

-If $\Sigma e^- \geq 14$ so the σz^L orbital is placed before the $\pi(x,y)^L$ orbital

VI-1-The bond order (bonding order) IL :

The bond order is a parameter that indicates whether a bond exists or not, as well as the nature of the bond.

The bond order is calculated using the expression:

► for the σ bond $IL_\sigma = \frac{\sum e^- \sigma - \sum e^- \sigma *}{2}$

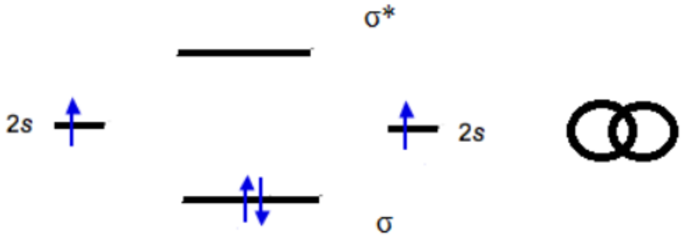
► for the π bond $IL_\pi = \frac{\sum e^- \pi - \sum e^- \pi *}{2}$

► The overall bond order $IL_\pi = \frac{\sum e^- bonding - \sum e^- antibondings}{2}$

Molecule Li_2 :

Li: $1s^2 2s^1$

2s – 2s interaction: necessarily axial σ bond.

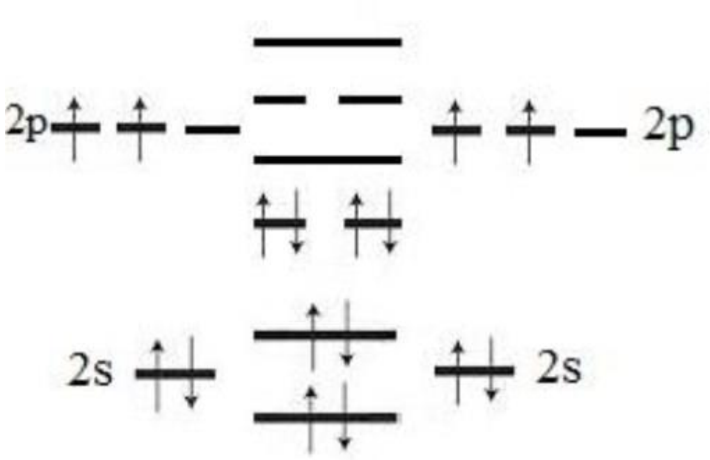


The bond order is IL= ½ (2 – 0) = 1 for Li_2.

Molecule C_2:

C: $1s^2 2s^2 2p^2$

Here, there are interactions2s – 2s, 2p – 2p et 2s – 2p. The correlation diagram of molecular orbitals is as follows:



Application to the molecule C_2 (with sp interaction)

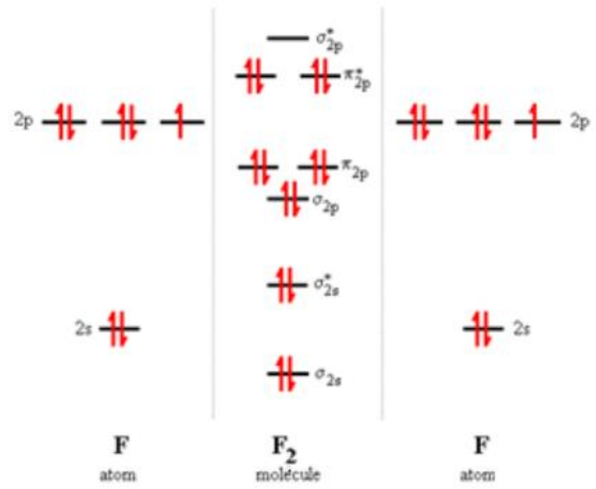
Bond order (bond index) IL = ½ (6 – 2) = 2.

The molecule does not possess any unpaired electrons and is diamagnetic. This is experimentally confirmed. If the sp interactions were not present, the molecule would have been paramagnetic (with 2 unpaired electrons)

If we remove an electron to form C_2^*, the molecule will be destabilized since it involves a bonding electron. The bond index will decrease, the bond length will increase, and the bond energy will decrease

Molecule F_2:

F: $1s^22s^2\ 2p^5$



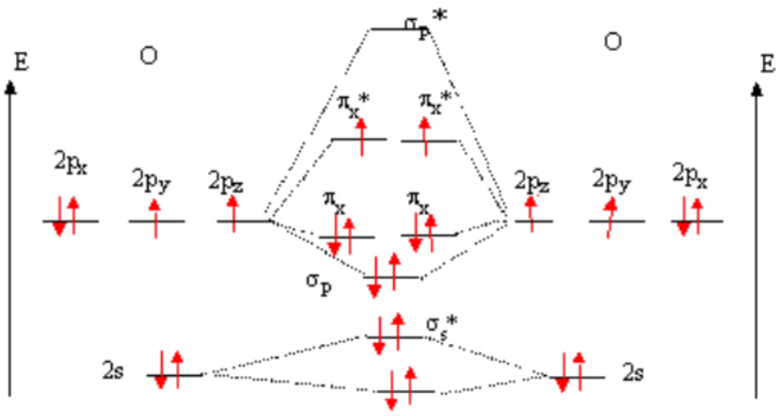
Application to the molecule F_2 (without sp interaction).

Bond index (bond order) IL = ½ (6 – 4) = 1.

Here again, removing an electron destabilizes the molecule.

Molecule O_2:

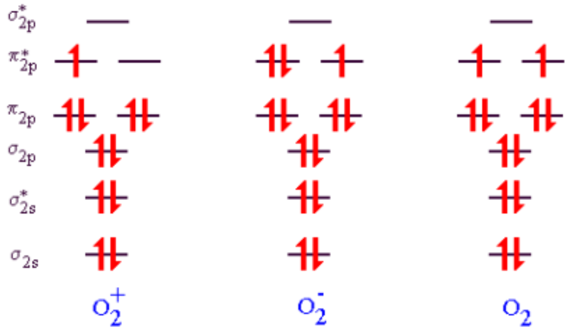
1- Energy diagram of the molecular orbitals (MO) of the homonuclear molecule O2 :



The electronic structure of O_2 is: $\sigma_s^2\ \sigma_s^{2*}\ \sigma_{pz}^2\ (\pi_x^2 = \pi_y^2)\ (\pi_x^{*1} = \pi_y^{*1})$

The bond index(bond order) is: $IL(O_2) = ½ (n – n^*) = ½ (8 – 4) = 2$

O: $1s^2\ 2s^2\ 2p^4$



IL (O_2) = ½ (n – n*) = ½ (8 – 4) = 2 The bond length L(O_2) = 1,21Å

IL (O_2^+) = ½ (n – n*) = ½ (8 – 3) = 2,5 The bond length L (O_2^+) = 1,12Å

IL (O_2^-) = ½ (n – n*) = ½ (8 – 5) = 1,5 The bond length L (O_2^-) = 1,26Å

IL (O_2^{2-}) = ½ (n – n*) = ½ (8 – 6) = 1 The bond length L (O_2^{2-}) = 1,49Å

As the bond index (bond order) increases, the bond length of these ions decreases

IL (O_2^+) >IL (O_2) >IL (O_2^-) >IL (O_2^{2-})

L (O_2^+) <L(O_2) <L(O_2^-) <L(O_2^{2-})

Application to the molecule O_2 (without sp interaction).

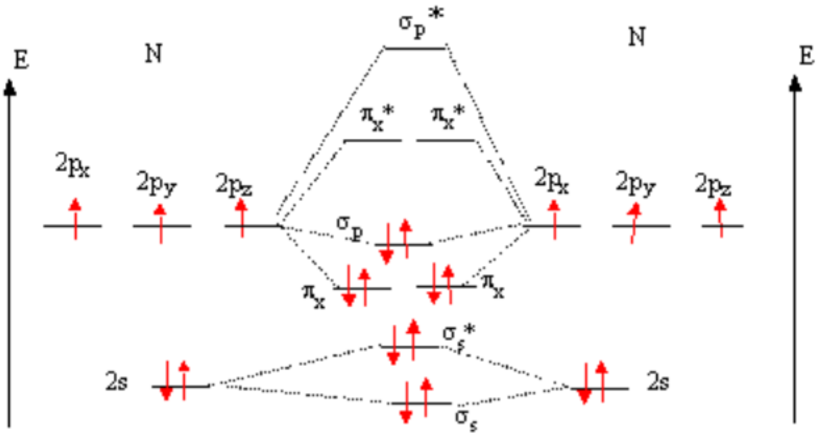
Bond index (bond order) IL = ½ (8 – 4) = 2.

The molecule possesses 2 unpaired electrons and is paramagnetic. This is confirmed experimentally

Example : Energetic diagram of molecular orbitals (MO) for the homonuclear molecule N2 (N: Z = 7).

There are interactions between the atomic s and p orbitals that involve an inversion of the molecular π_x and π_y orbitals, along with the molecular σ_{px} orbital.

N: $1s^2\ 2s^2\ 2p^3$



The electronic structure of the N2 molecule is : $\sigma s^{2}\ \sigma_s^{2*}\ (\pi_x^{2} = \pi_y^{2})\ \sigma_{px}^{2}$

Energetic diagram of molecular orbitals (MO) for the heteronuclear CN molecule.

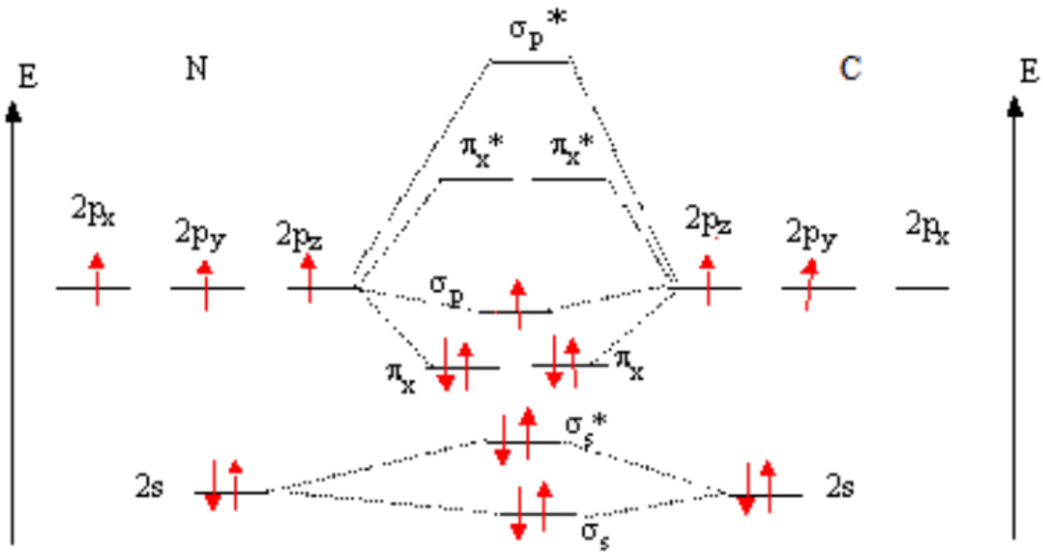
For heteronuclear molecules formed from atoms of the second period of the periodic table, there are interactions between the atomic s and p orbitals that involve an inversion of the molecular π_x and π_y orbitals, along with the molecular σ_{pz} orbital

N: $1s^2\ 2s^2\ 2p^3$

C: $1s^2\ 2s^2\ 2p^2$

The nitrogen atom N is more electronegative than the carbon atom. Therefore, the energy values of the nitrogen atomic orbitals are lower than those of carbon

The energy diagram in this case is asymmetrical.



The electronic structure of the CN molecule is: $\sigma_s^2\ \sigma_s^{2*}\ (\pi_x^2 = \pi_y^2)\ \sigma_{px}^1$

Magnetic Properties of N_2 and CN.

The presence of a single electron in the molecular orbitals of CN makes this molecule paramagnetic. In contrast, in the N2 molecule, the electrons are paired, giving N_2 a diamagnetic character.

VII- Application Exercise

Exercise N° 01:

Represent the bonds in the following molecules or ions: H_2O, NH_3, NH_4^+, N_2, H_2CO_3 and SO_4^{2-}.

Exercise N° 02:

Consider the following molecules:

CH_4, C_2H_4, C_2H_2, CH_3COOH, CH_3OH, C_6H_5-CH-OH, CO-CH_3 and CO_2.

Indicate an appropriate hybridization for the valence orbitals of the central atoms of each molecule.

1- Predict the shape of each molecule.

2- Describe and name all types of bonds involved in each molecule**.**

Exercise N° 03 :

Indicate an appropriate hybridization for the valence orbitals of the central atom and predict the shape of the following molecules: CS_2, BeH_2, BCl_3, ClO_4^- and $AlCl_6^{3-}$.

Exercise N° 04 :

Give the energy diagram of the molecular orbitals for the oxygen molecule O_2.

Exercise N° 05 :

1- Draw the energy diagrams corresponding to the different molecules: Li_2, Be_2, C_2, N_2 and F_2.

2- Determine the bond order of each molecule.

3- What can be concluded?

4- Give the electronic configurations of the different molecules**.**

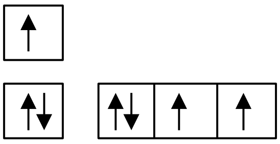
Solution :

Solution N°01:

H_2O:

H (Z =1) $1s^1$

O (Z = 8) $1s^2$ $2s^2$ $2p^4$

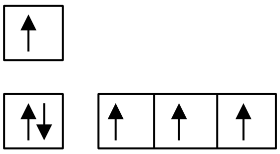


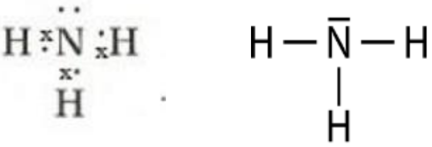
There are 2 covalent bonds; to satisfy the octet rule, the 2 electrons come from 2 hydrogen atoms.

NH_3:

H (Z =1) $1s^1$

N (Z =7) $1s^2$ $2s^2$ $2p^3$

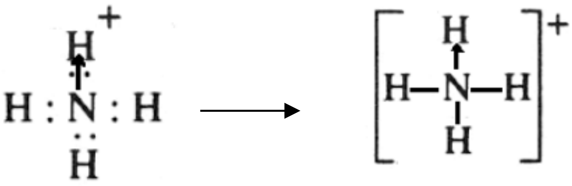




3 covalent bonds; this lone pair is the source of the basic properties of the ammonia molecule..

NH_4^+:

3 covalent bonds and one dative bonds.



N_2:

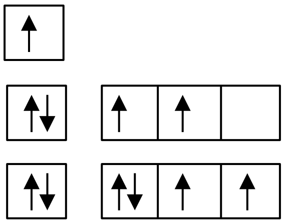
3 covalent bonds between the 2 nitrogen atoms.

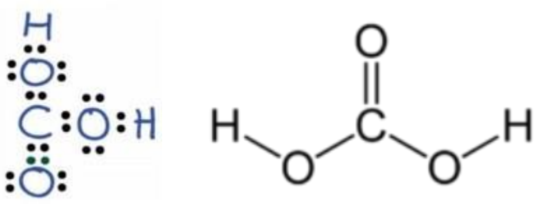
H_2CO_3:

H (Z =1) $1s^1$

C (Z = 6) $1s^2\ 2s^2\ 2p^2$

O (Z = 8) $1s^2\ 2s^2\ 2p^4$



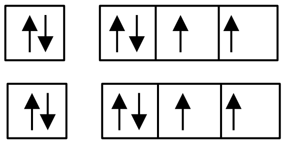


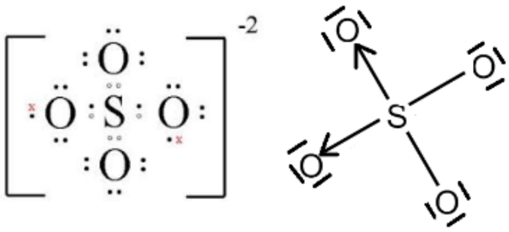
After hybridization, carbon is capable of forming 4 covalent bonds. There is a double bond between C and O (sp2 hybridization for C). There are two single bonds between the carbon atom and the 2 oxygen atoms..

SO_4^{2-}:

S (Z = 16) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

O (Z = 8) $1s^2\ 2s^2\ 2p^4$

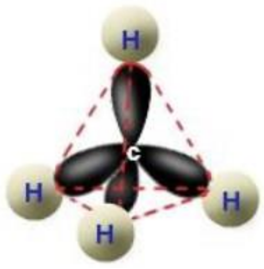




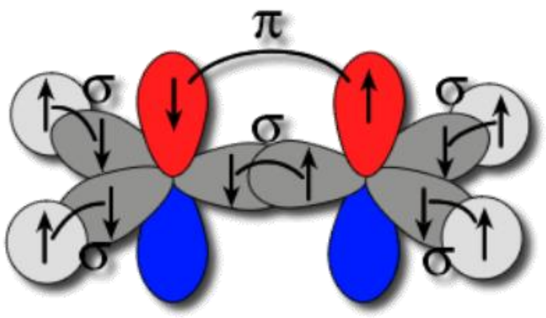
Sulfur has 2 unpaired electrons, thus forming 2 covalent bonds with 2 oxygen atoms. The 2 lone pairs of sulfur would be shared with oxygen, which is an electronegative element (semi-polar bonds). The representations do not account for the geometry of the molecules.

Solution N°02:

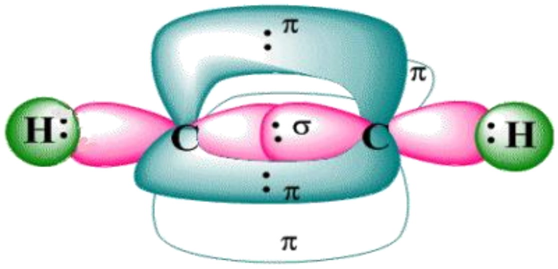
CH_4: sp3 hybridization, tetrahedral shape, 4 σ bonds.



C_2H_4: sp2 hybridization, planar shape.

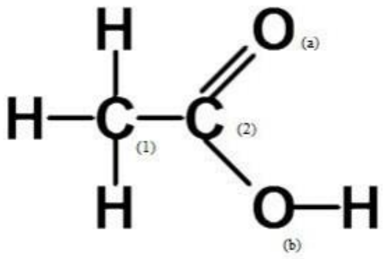


C_2H_2: sp hybridization, linear shape..



H—C≡C—H

CH_3COOH:



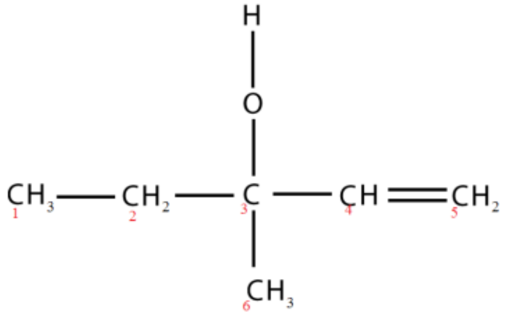
1) sp^3 hybridization, 4 bonds σ (corner 109°,5').
2) Sp^2 hybridization, 3 bonds σ (corner 120°).

$O_{(a)}$ a orbital p_y, $O_{(b)}$ a hybridized orbital.

π bond between C_2 and O through lateral pz overlap … hybridized

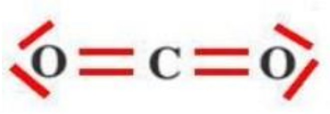
CH_3OH: sp^3 hybridization , 4 bonds σ.

C_6H_5-CH-OH: sp^3 hybridization for C1, C2, C3 et C6, sp^2 hybridization for C4, C5.



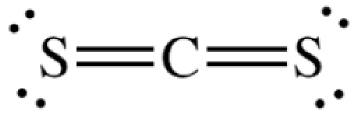
CO-CH_3:

CO_2: 2 bonds σ and 2 bonds π, hybridization sp linear molecule.

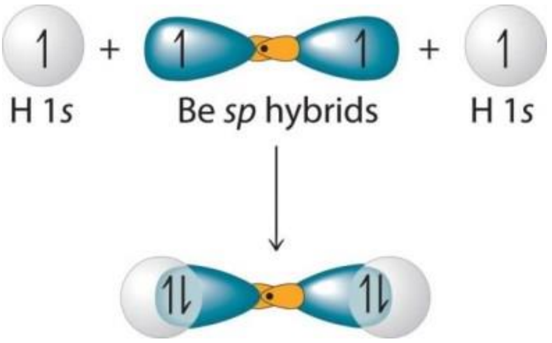


Solution N°03:

CS_2: 2 sp hybridized orbitals, linear shape



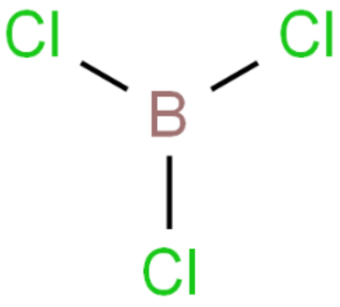
BeH_2: sp hybridized, linear shape.

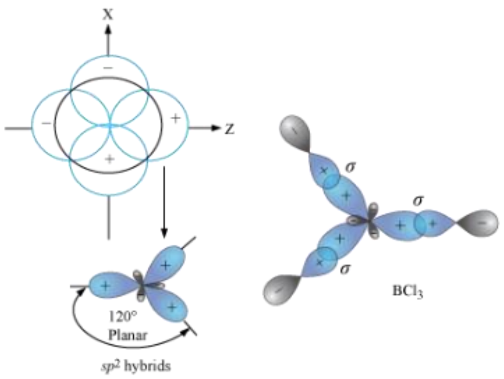


BCl_3: trigonal planar shape.

B $1s^2 2s^2 2p^1$	↑↓	↑			⇔	↑	↑	↑

sp²

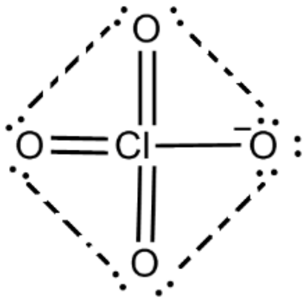




ClO_4^-: The 4 hybridized orbitals for σ bonds are sd³, and 3 p orbitals form the π bonds between Cl and O.Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

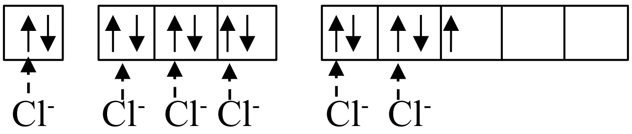
↑↓	↑↓	↑↓	↑	3d³				
↑	↑	↑	↑	↑	↑	↑		

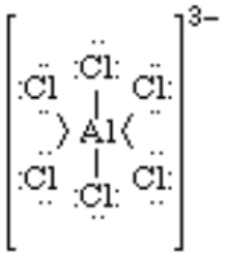
$p_x \quad p_y \quad p_z$



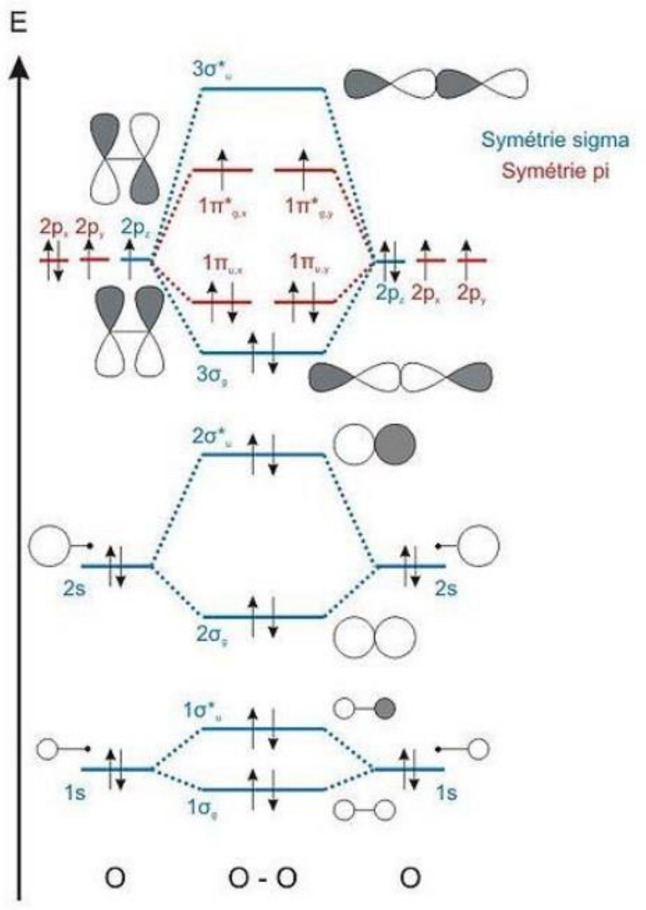
$AlCl_6^{3-}$: 6 sp³d² hybrid orbitals, octahedral

$_{13}Al^{3-} \quad 1s^2\ 2s^2\ 2p^6\ \cancel{3s^2}\ \cancel{3p^1}$





Solution N°04:



electronic configuration d’O_2.

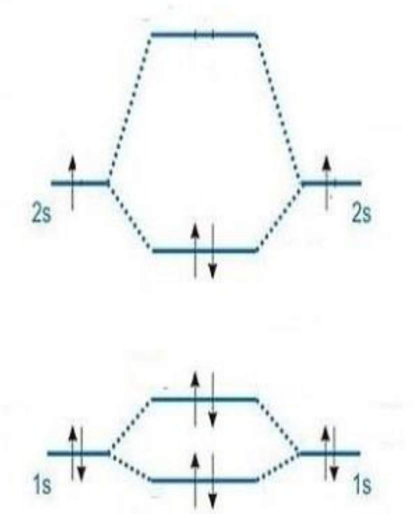
$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2pz})(\pi_x)^2(\pi_y)^2(\pi_x^*)(\pi_y^*)$

Solution N°05:

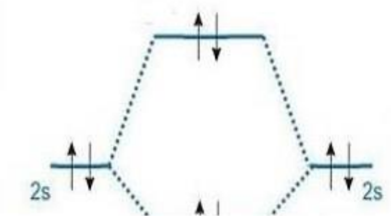
Li_2:

Electronic structure of the Li atom: $1s^2\ 2s^1$

Energy diagram of Li:



Be_2:



Electronic structure of the Be atom: $1s^2\ 2s^2$

Energy diagram of Be_2:

C$_2$:

Electronic structure of the C: $1s^2\ 2s^2\ 2p^2$

Energy diagram of C_2:

Note

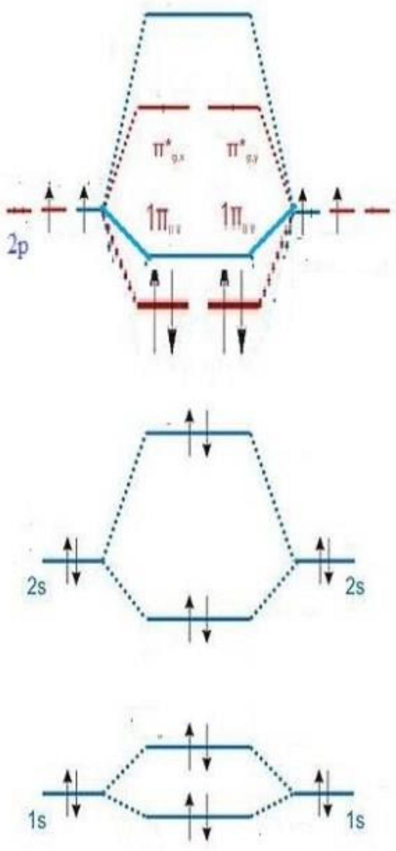
The σz level moves above the πx and πy levels.

Hence the interaction between the σs and σz levels.

This is valid whenever

the number of electrons contributed by the two atoms

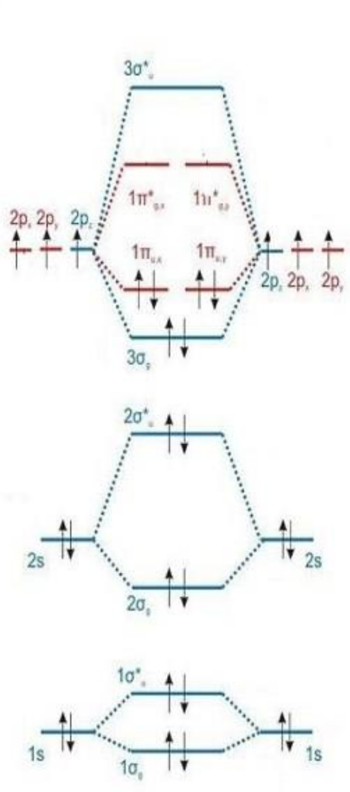
is less than or equal to fourteen (14 e-)



N_2:

Electronic structure of the N: $1s^2\ 2s^2\ 2p^3$

Energy diagram of N_2: (Nombre total $e^- = 14$).



F_2:

Electronic structure of the F: $1s^2\ 2s^2\ 2p^5$

Energy diagram of F_2: (Nombre total $e^- > 14$).

The total number of electrons contributed by the two fluorine atoms is 18 (>14), so there will be no interaction between the σz and σs levels. Thus, the σ level remains below the πx and πy levels.

I- First law of thermodynamic:

I-1-Definition:

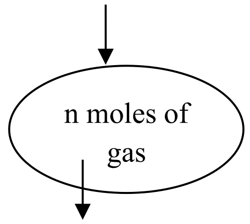
Thermodynamics is the study of Calorific phenomena that accompany different chemical reactions, including:

- Various exchanges of physical states.
- Exchanges of energy, heat quantities, and work.
- Formation of solution.
- Heating or cooling operations.

I-2-Thermodynamic System

In thermodynamics, the system to be studied can be defined as a part of the universe, while the rest is called: the external environment.

Thermodynamic System



External environment (also we can say: surroundings)

There are three types of systems :

a) Isolated System: This is a system where there is no exchange of heat or matter.

b) Closed System: In this system, there is an exchange of heat but not of matter.

c) Open System: This is a system where there is an exchange of both heat and matter.

II- Statement of the First Law:

The First Law states that the internal energy of a system cannot be created or destroyed spontaneously. Thus, the energy of an isolated system remains constant. This is the principle of conservation of energy.

During a chemical transformation, the change in internal energy represents the algebraic sum of the work done and the quantity of heat exchanged during that transformation.

$$\Delta U = W + Q$$

Where : ΔU : Change in internal energy expressed in (Calorie or Joule)

W : Work expressed in (Joule)

Q : (Quantity of heat expressed in (calorie)

II-1- The quantity of heat (heat quantity) (Q) :

It is either in the form of energy:

- Electrical.
- Mechanical (transformation).
- Nuclear => into heat energy (calorific)

It is given by the expression :

$$Q = n \times C \times \Delta T$$

$$Q = m \times C' \times \Delta T$$

Where C : Molar heat capacity or molar specific heat (Cal/ mol c°)

C' : Mass heat capacity or mass specific heat (Cal/ g c°).

We can define the heat capacity or specific heat of a substance as the amount of heat required to raise the temperature of one gram or one mole of that substance by 1 degree Celsius .

II-2- Work (W) :

The expression of work in mechanics is given by the product of force (F) and displacement (l), thus by the relation: **$W = F.\,l$**

Pressure is given by : $P = \frac{F}{S}$ (F perpendicular to S) then force : $F = P x S$

So :**$W = PxSxl = PxV$** with $V = S \times l$

- W : work (J) Joule.
- F : Force (N) Newton, N : unit of force.
- S : Surface area (m^2).
- P : Pressure (Pa) Pascal $1N/m^2$.
- V : volume (m^3).

In thermodynamics, and for a gaseous system, work can be expressed by the relation:

For an infinitesimal transformation:**$dW = PxdV$**

So the overall work : $$W = -\int_{V_i}^{V_f} PdV$$

For a gas, there are 2 cases:

► Compression:

$$\boxed{V_1} \longrightarrow \boxed{V_2}$$

$V_2 < V_1$

$$W = -\int_{V_i}^{V_f} PdV = -P\int_{V_i}^{V_f} dV = -P\underset{W > 0}{\overset{< 0}{(V_2 - V_1)}}$$ So : **$W > 0$**

► Expansion:

$$\boxed{V_1} \longrightarrow \boxed{V_2}$$

$V_2 > V_1$

$$W = -\int_{V_i}^{V_f} PdV = -P\int_{V_i}^{V_f} dV = -P\underset{W<0}{\overset{>0}{(V_2 - V_1)}} \text{ So: } \mathbf{W} < 0$$

The ideal gas law: **PV = nRT**

P : Pressure in atm, P_a, mmHg.

V: Volume in L, m^3.

n: Number of moles.

T: Temperature in kelvin.

R: Ideal gas constant.

$$\begin{cases} R = 0{,}082\ Latmmol^{-1}k^{-1} \\ R = 8{,}31J\ k^{-1}mol^{-1} \\ R = 2cal\ k^{-1}mol^{-1} \end{cases}$$

III- Change in internal energy:

$\Delta U = U_f - U_i$

U : Internal energy, it depends on temperature T.

If $T = C^{ste} \Rightarrow U = C^{ste} \Rightarrow \Delta U = 0$

For an isolated system: $\Delta U = 0$ thus: $U_f = U_i$

If $\Delta U>0$ the system gains energy.

If $\Delta U<0$ the system releases energy.

This energy change between the system and the surroundings (the external environment) occurs either in the form of work (W) or in the form of heat (Q), or both: W and Q

⇨ Quasi-static or reversible transformation.

The transformation is reversible if it is achievable in both directions, meaning it is quasi-static :

In thermodynamics, a chemical reaction is accompanied by an energy transformation involving heat and work, depending on state parameters: P, V, T°. There are various types of transformations

If temperature is constant ⟶ it's an isothermal transformation.

If pressure is constant ⟶ it's an isobaric transformation.

If volume is constant ⟶ it's an isochoric transformation.

If heat exchange is zero ⟶ it's an adiabatic transformation.

III-1- Isobaric transformation P = cste :

$P = \text{cste} \Rightarrow W = -\int_{V_i}^{V_f} PdV = -P\int_{V_i}^{V_f} dV = -P(V_f - V_i)$

$\Delta U = Q + W$

$\Delta U = Q_P - P\,(V_f - V_i)$

$U_f - U_i = Q_P - P\,(V_f - V_i)$

$U_f - U_i = Q_P - PV_f + PV_i$

$U_f - U_i + PV_f - PV_i = Q_P$ We define H = U + PV => Enthalpy

$\underbrace{(U_f + PV_f)}_{H_f} - \underbrace{(U_i + PV_i)}_{H_i} = Q_P = n.\,C_P.\,\Delta T$

Therefore: $\boxed{}$ **$Q_P = \Delta H = n.\,C_P.\,\Delta T$**

C_P : Molar heat capacity at constant pressure or molar specific heat at constant pressure.

ΔH : Enthalpy change.

Si ΔH°<0 exothermic reaction.

Si ΔH°> 0 endothermic reaction.

Si ΔH°= 0 athermal reaction.

At constant pressure, the change in enthalpy represents the amount of heat exchanged with the surroundings.

III-2- Isochoric transformation V = cste :

Si V = cste =>$W = -\int PdV = 0$ because $V_f = V_i$

$\Delta U = Q + \underbrace{W}_{0}$ => **$\Delta U = Q_V = n.\ C_V.\ \Delta T.$**

C_V : Molar heat capacity at constant volume or Molar heat capacity at constant volume.

At constant volume, the change in internal energy represents the amount of heat exchanged with the surroundings.

III-3- Isothermal transformation T = cste :

If T = cste => U = cste => $\Delta U = U_f - U_i = 0$

So : $\Delta U = Q + W = 0$

$Q_T = - W$

We have : $W = -\int PdV$

According to the ideal gas law:

$$PV = nRT \Rightarrow P = \frac{nRT}{V}$$

$$W = -\int_{V1}^{V2} \frac{nRT}{V} dV$$

$$W = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow W = -nRT \ln V \,|_{V_1}^{V_2} = -nRT\,(\ln V_2 - \ln V_1)$$

$$\mathbf{W = -nRT \ln \frac{V_2}{V1}} \quad \mathbf{Q_T = -nRT \ln \frac{V_2}{V1}}$$

We have: $V_1 = \frac{nRT}{P_1}$, $\quad V_2 = \frac{nRT}{P_2}$

We can write : $\mathbf{W = -nRT \ln \frac{P_1}{P_2}} \quad \mathbf{Q_T = -nRT \ln \frac{P_1}{P_2}}$

At constant temperature, work represents the amount of heat exchanged with the surroundings.

III-4- Meyer's relation :

Meyer's relation establishes the connection between the specific heat at constant pressure, C_P, and the specific heat at constant volume, C_V.

Based on the enthalpy relation $H = U + PV$

$\Delta H = \Delta U + \Delta(PV)$

$Q_P = Q_V + \Delta(PV)$

$n.\ C_P.\ \Delta T = n.\ C_V.\ \Delta T + \Delta(nRT)$

$\cancel{n}.\ C_P.\ \cancel{\Delta T} = \cancel{n}.\ C_V.\ \cancel{\Delta T} + \cancel{n}R\cancel{\Delta T}$

This leads to Meyer's relation: $\boldsymbol{C_P = C_V + R}$

The relation between the quantity of heat at constant pressure, Q_P, and the quantity of heat at constant volume, Q_V,

$\Delta H = \Delta U + \Delta(PV)$

$Q_P = Q_V + \Delta(PV)$ and $PV = nRT$

$\boldsymbol{Q_P = Q_V + \Delta n\ RT}$

Δn : represents the change in stoichiometric coefficients of gases.

$$\Delta n = \sum \text{cœff}_{\text{product gases}} - \sum \text{cœff}_{\text{reactant gases}}$$

Example:

Consider the reaction: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$\Delta n = 1 - 1 = 0$

$Q_P = Q_V$

Consider the reaction: $H_{2(s)} + S_{(S)} + 2O_{2(g)} \longrightarrow H_2SO_{4(l)}$

$Q_P = Q_V + \Delta n\ RT$

$\Delta n = 0 - 3 = -3$

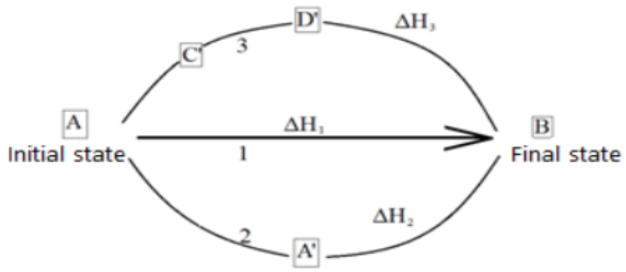
$Q_P = Q_V - 3RT$

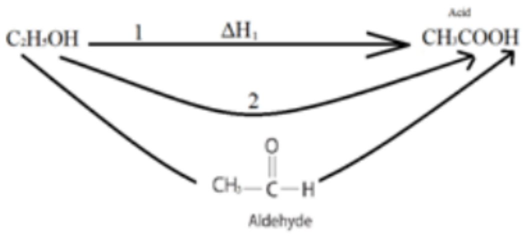
IV-HESS's law :

A thermodynamic parameter is called a state function if it depends only on the initial and final states.

Ex : we have : $\Delta H_1 = \Delta H_2 = \Delta H_3$

ΔH is a state function





The change in enthalpy for a chemical reaction is equal to the difference between the sum of the enthalpies of the products and reactants :

$$\Delta H_r = \sum \Delta H_{f\ products} - \sum \Delta H_{f\ reactants}$$

Note : The change in enthalpy for pure simple substances is zero.

ΔH_f(pure simple substances) = 0

$H_{2(g)}$, $Cl_{2(g)}$, $N_{2(g)}$, $O_{2(g)}$,$C_{(s)}$, $Fe_{(s)}$, $Na_{(s)}$.

Ex:

$$C_3H_6O_2 + \frac{7}{2}O_2 \longrightarrow 3CO_2 + 3H_2O$$

$$\Delta H_r = \sum \Delta H_{f\ products} - \sum \Delta H_{f\ reactants}$$

$$\Delta H_r = 3\Delta H_{f(CO_2)} + 3\Delta H_{f(H_2O)} - \Delta H_{f(C_3H_6O_2)} - \frac{7}{2}\cancel{\Delta H_{f(O_2)}}$$

0 Pure simple substance (pure element)

Standard state:

A substance is in its standard state when it is in its pure state at a pressure of 1 atmosphere and a temperature of 25°C.

T = 25°C = 25 + 273 = 298k.

The standard enthalpy change is denoted as: $\Delta H°_{298}$: standard enthalpy change.

Example:

Determine the ΔH° for the following reaction:

$SO_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow SO_{3(g)}$ $\Delta H° = ?$

Given:

$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$ $\Delta H°_1 = -70{,}96$ kcal

$S_{(s)} + 3/2\ O_{2(g)} \longrightarrow SO_{3(g)}$ $\Delta H°_2 = -94{,}48$ kcal

We reverse the first reaction

$SO_{2(g)} \longrightarrow S_{(s)} + O_{2(g)}$ $-\Delta H°_1$

$\cancel{S}_{(s)} + 3/2\ O_{2(g)} \longrightarrow SO_{3(g)}$ $\Delta H°_2$

$SO_{2(g)} + 3/2\ O_{2(g)} \longrightarrow O_{2(g)} + SO_{3(g)}$

$SO_{2(g)} + ½O_{2(g)} \longrightarrow SO_{3(g)}$

$\Delta H° = - \Delta H°_1 + \Delta H°_2 = 70{,}96 - 94{,}48 = - 23{,}52$ kcal

$\Delta H° < 0$ exothermic reaction.

V- Variation of enthalpy with temperature: KIRCHHOFF's Law:

Consider a reaction: $A \longrightarrow B \quad \Delta H_1 (T_1)$

Knowing the variation of ΔH for a reaction at T_1, we can deduce the variation of ΔH for the same reaction at T_2. Let ΔH_T represent the variation of ΔH at temperature T

ΔH_{T+dT} variation of ΔH at temperature T+dT

$$\begin{tikzcd}
A \arrow[r] \arrow[d, swap, "T \ \Delta H1"] & B \\
A \arrow[r, swap, "T+dT^{\Delta H2}"] & B \arrow[u, swap, "T \ \Delta H3"]
\end{tikzcd}$$

$\Delta H_T = \Delta H_1 + \Delta H_{T+dT} + \Delta H_3$

Expression of ΔH in terms of C:

$\Delta H_1 = C_A \Delta T = C_A(T_2 - T_1) = C_A(T+dT - T) = C_A dT$

$\Delta H_1 = T+dT$

$\Delta H_3 = C_B \Delta T = C_B (T - T - dT) = - CB \ dT$

$\Delta H_T = C_A dT + T + dT - C_B dT$

$\Delta H_T = \Delta H_{T+dT} + (C_A - C_B) \ dT$

$\Delta H_{T+dT} = \Delta H_T - (C_A - C_B) \ dT$

$\Delta H_{T+dT} = \Delta H_T + (C_B - C_A) \ dT$

ΔH_{T+dT}-ΔH_T= $(C_B - C_A)$ dT

$$\int_{T}^{T+dT} d(\Delta H) = \int (C_B - C_A)\, \mathrm{dT}$$

$$\mathbf{\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_P dT}$$

With : $\Delta C_P = \sum C_{P\ \text{products}} - \sum C_{P\ \text{reactants}}$

Example 1 : Synthesis of Ammonia NH_3

$$\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftarrows NH_3$$

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

At T_1 = 25°C, we have : ΔH_1= -44,2 Kcal/mol. Calculate ΔH_2à T_2 = 50°C ?

Given :

C_p (N_2) = 3,6 cal/mol.

C_p (H_2) = 8,2 cal/mol.

C_p (NH_3) = 2,5 cal/mol.

1) Calculation of $\Delta C_P = \sum C_{P\ \text{products}} - \sum C_{P\ \text{reactants}}$

$$\Delta C_P = 2C_{P(NH_3)} - (3C_{P(H_2)} + C_{P(N_2)})$$

$$\Delta C_P = 2C_{P(NH_3)} - 3C_{P(H_2)} - C_{P(N_2)}$$

$$\Delta C_P = 2(2{,}5) - 3(8{,}2) - (3{,}6)$$

$$\Delta C_P = 5 - 24{,}6 - 3{,}6$$

$$\Delta C_P = -23{,}2\frac{cal}{mol}.$$

$T_1 = 25°c = 298$ K

$T_2 = 50°c = 323$ K

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_P dT$$

$$\Delta H_{323} = \Delta H_{298} + \int_{298}^{323} \Delta C_P dT$$

$$\Delta H_{323} = \Delta H_{298} + \Delta C_P \int_{298}^{323} dT$$

$$\Delta H_{323} = -44{,}2 \text{ x } 10^3 - 23{,}2 \int_{298}^{323} dT$$

$$\Delta H_{323} = (-44{,}2 \text{ x } 10^3) - 23{,}2\ (323 - 298)$$

$$\Delta H_{323} = -44780 \frac{\text{cal}}{\text{mol}}.$$

Special Case: If Cp values are temperature-dependent

Same example :

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

At $T_1 = 25°c\ \Delta H_1 = 54{,}3 \frac{\text{cal}}{\text{mol}}$.

Calculate ΔH_2 ($T_2 = 150°C$)

$C_P (N_2) = 2{,}3\ T^2 - 5T + 8$

$C_P (H_2) = 4\ T^2 - 3T$

$C_P (NH_3) = T^2 - 8T + 12$

$$\Delta C_P = \sum C_{P\ \text{products}} - \sum C_{P\ \text{reactants}}$$

$$\Delta C_P = 2(T^2 - 8T + 12) - 3(4T^2 - 3T) - (2{,}3T^2 - 5T + 8)$$

$$\Delta C_P = -12{,}3T^2 - 2T + 16 \text{ Cal/mol.}$$

$$\Delta H_{423} = \Delta H_{298} + \int_{298}^{423} \Delta C_P dT$$

$$\Delta H_{423} = 54{,}3x10^3 + \int_{298}^{423} (-12{,}3T^2 - 2T + 16)dT$$

$$\Delta H_{423} = 54{,}3x10^3 - 12{,}23 \int_{298}^{423} T^2 dT - 2 \int_{298}^{423} TdT + \int_{298}^{423} dT$$

$$\Delta H_{423} = 54{,}3x10^3 - 12{,}23 \left(\frac{T^3}{3}\right)_{298}^{423} - 2 \left(\frac{T^2}{2}\right)_{298}^{423} + 16(T)_{298}^{423}$$

$$\Delta H_{423} = 54{,}3x10^3 - 12{,}23 \left(\frac{(42\ \ )^3 - (298)^3}{3 \quad 3}\right) - 2 \left(\frac{(423)^2 - (29\ \ )^2}{2 \qquad 8}\right)$$

$$+ 16(423 - 298)$$

$$\Delta H_{423} = -2{,}018 \text{ x } 10^8 \text{ Cal/mol}$$

$$\Delta H_{423} = -2018 \text{ x } 10^2 \text{ KCal/mol}$$

Application example: ΔH_{1300k}

$H_{2(g)} + ½\ O_{(g)} \longrightarrow H_2O_{(g)}$

Given the molar heat capacities (heats of mass) are as follows:

$C_P(H_2)$ =3,5 cal/gr. $C_P(O_2)$ = 0,22 cal/gr. $C_P(H_2O)$= 0,49 cal/gr

ΔH_{300k} = - 57,8 kcal

Determining molar heat capacities C_P:

$C_P(H_2)$ = 3,5 x2 = 7 cal/mol $C_P(O_2)$ = 0,22 x 32 = 7,04 cal/mole $C_P(H_2O)$ = 0,49 x 18 = 8,82 cal/mole

$$\Delta H_{1300k} = \Delta H_{300k} + \int_{300}^{1300} (0{,}49\,.18) - 7 - (\tfrac{1}{2}\,.0{,}22\,.32)\, dT$$

$\Delta H_{1300k} = \Delta H_{300k} = 57800 + (0{,}49\ .18) - 7 - (\frac{1}{2}\ .0{,}22\ .32)\ .(1300 - 300)$

57,8 kcal = 57800 cal

ΔH_{1300k} = - 59500 cal exothermic reaction.

Practice exercises:

Exercise N°1 :

A mass of 10g of nitrogen (N_2) undergoes an isobaric transformation from state 1 (P_1 = 1,5 atm, T_1 = 80°C), to state 2 (T_2 = 120°C). When 2085 J of heat are added to the system, it performs work of 810 J (W<0 (W = -810J)).

1) Calculate the initial state volume V1.
2) Calculate the final state volume V2.
3) Calculate ΔH, ΔV.

Given : C_P = 8,2 Cal/mol. M (N_2) = 28 g/mol

$\text{State 1} \xrightarrow{\text{Isobaric}} \text{State 2}$

P_1 = 1,5 atm P_2 = 1,5 atm

T_1 = 353 K T_2 = ?

V_1 = ? V_2 = ?

$$n = \frac{m}{M} = \frac{10}{28} = 0{,}36\text{mole}$$

$$P_1V_1 = nRT_1 \Rightarrow V_1 = \frac{nRT_1}{P_1} = \frac{0{,}36 \text{ x } 0{,}\ \ 82 \text{ x } 353}{10{,}5} = 6{,}95\text{L}$$

Calculating V_2 and T_2 ?

$$W = -\int PdV \Rightarrow W = -P\int_{V_1}^{V_2} dV$$

$$W = -P(V_2 - V_1)$$

$$W = -PV_2 + PV_1 => V_2 = \frac{PV_1 - W}{P} = \frac{-W}{P} + V_1$$

$$V_1 = 6{,}95L = 6{,}95 \text{ x } 10^{-3}m^3$$

$$P = 1{,}5 \text{ atm} = 1{,}5\ 10^5 \text{ Pa}$$

$$V_2 = V_1 - \frac{W}{P} => V_2 = 6{,}95 \text{ x } 10^{-3}m^3 — 810\ /1{,}5\ 10^5 \text{ Pa}$$

$$V_2 = 1{,}23 \text{ x } 10^{-3}m^3 => V_2 = 12{,}3 \text{ L}$$

$$P^2V^2 = nRT^2 => T^2 = \frac{P_2V_2}{nR} = \frac{1{,}5 \text{ x } 12{,}3}{0{,}36 \text{ x } \overset{0}{}{,}082} = 625 \text{ K}$$

Calculating ΔH (P = cste)

$\Delta H = Q_P = n\ C_P\ \Delta T$

$\Delta H = Q = 2025$ J

Calculating ΔU

$\Delta U = W + Q$

$\Delta U = -810 + 2025 = 1215$ J

Deriving the value of C_V.

$C_P = C_V + R$ $C_P = 8{,}2$ Cal/mol

$C_V = C_P - R$

J ($R = 8{,}31$ J k^{-1} mol^{-1})

Cal ($R = 2$ Cal k^{-1} mol^{-1})

$C_V = 8{,}2 - 2 = 6{,}2$ Cal/mol.

Calculating the amount of heat Q.

$Q_V = n\, C_V \Delta T = 0{,}36 \times 6{,}2 \times (625 - 353) = 607{,}1$ Cal

Exercise N°2:

Let's consider the combustion reaction of $C_3H_8O_2$

$C_3H_8O_2 + 4O_2 \longrightarrow 3CO_2 + 4H_2O$

$\Delta H_r = -35{,}8$ Kcal/mol.

Given:

a) $CO_2 \longrightarrow C_{(s)} + O_{2(g)}$ $\Delta H_a = 22$ Kcal/mol.

b) $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H_b = -25$ Kcal/mol.

c) $C_{(s)} + O_{2(g)} + H_{2(g)} \longrightarrow C_3H_8O_2$ $\Delta H_c = -115$ Kcal/mol. verify balance

1) Calculate ΔH_r at T = 25°C

2) Deduce the value of ΔH2 à $T_2 = 100$°C

$C_P(H_2O) = 4{,}15$ cal/mol. $C_P(CO_2) = 3{,}12$ cal/mol.

$C_P(C_3H_8O_2) = -12{,}5$ cal/mol. $C_P(O_2) = 4{,}9$ cal/mol.

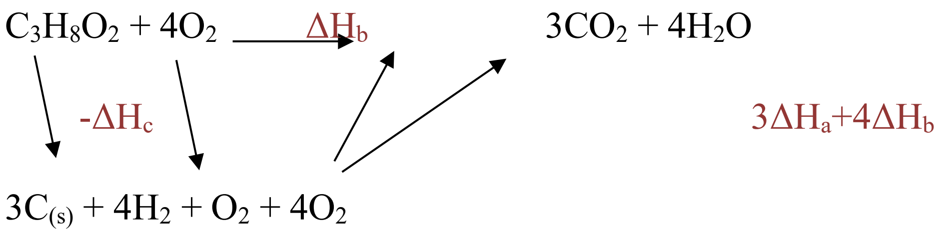
$$\Delta H_r = \sum \Delta H_{f\ products} - \sum \Delta H_{f\ reactants}$$

$$\Delta H_r = 3\Delta H_{f(CO_2)} + 4\Delta H_{f(H_2O)} - \Delta H_{f(C_3H_8O_2)} - 4\Delta \cancel{H_{f(O_2)}}$$

$$\Delta H_{f(C_3H_8O_2)} = 3\Delta H_{f(CO_2)} + 4\Delta H_{f(H_2O)} - \Delta H_r \quad at\ T = 25°c$$

$\Delta H_{f(C_3H_8O_2)}$ $at\ T = 100°c$ We apply Kirchhoff's law:

$$\Delta H_{373} = \Delta H_{298} + \int_{298}^{373} \Delta C_P dT$$



a) $3(C_{(s)} + O_{2(g)} \longrightarrow CO_2)$ $-\Delta H_a \times 3$

b) $4(H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)})$ $\Delta H_b \times 4$

c) $C_3H_8O_2 \longrightarrow 3C_{(s)} + 4H_{2(g)} + O_{2(g)}$ $-\Delta H_c$

$3C_{(s)} + 3O_{2(g)} \longrightarrow 3CO_2 - 3\Delta H_a$

$4H_{2(g)} + 2O_{2(g)} \longrightarrow 4H_2O_{(l)}$ $4\Delta H_b$

$C_3H_8O_2 \longrightarrow 3C_{(s)} + 4H_{2(g)} + O_{2(g)}$ $-\Delta H_c$

$C_3H_8O_2 + 4O_2 \longrightarrow 3CO_2 + 4H_2O$

$$\Delta H_r = -3\Delta H_a + 4\Delta H_b - \Delta H_c$$

VI- Expressions of reaction enthalpy:

In thermodynamics, there are several types of reactions for which we define a change in enthalpy ΔH.

VI-1- Enthalpy of formation (ΔH_f):

The enthalpy of formation is the energy required to form one mole of a compound from its constituent elements in their standard states (pure elements).

Ex :

$H_2 + Cl_2 \longrightarrow 2HCl$ $\Delta H_r = 2\Delta H_{f(HCl)} - \overset{0}{\cancel{\Delta H_{f(H_2)}}} - \overset{0}{\cancel{\Delta H_{f(Cl_2)}}}$ pure elements

$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O\,\Delta H_r$

$$S + H_2 + 2O_2 \longrightarrow H_2SO_4$$

$$\underbrace{C + O_2}_{\text{Pure element}} \longrightarrow \underbrace{CO_2}_{\text{compound}}$$

VI-2- Bond enthalpy (bond energy E_L or ΔH_L) :

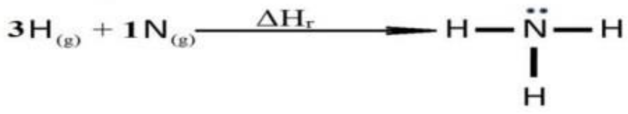
Bond enthalpy is the energy required to break a bond between two gaseous atoms.

ΔH_L is always negative: $\Delta H_L < 0$

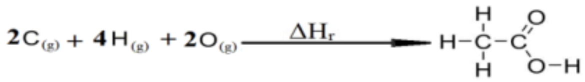
Dissociation Enthalpy ($\Delta H_{dissociation} = -\Delta H_L > 0$)

Example :

$H_{(g)} + Cl_{(g)} \longrightarrow \Delta H_L$ **H–Cl** $\Delta H_r = \Delta H_{L\,(H–Cl)}$



$\Delta H_r = 3\Delta H_{L\,(N-H)}$



$$\Delta H_r = 3\Delta H_{L\,(C-H)} + \Delta H_{L\,(C-C)} + \Delta H_{L\,(C=O)} + \Delta H_{L\,(C-O)} + \Delta H_{L\,(O-H)}$$

Some bond energy values

Bond	Cl-Cl	Br-Br	I-I	H-Cl	H-Br	H-I
Bond Energy kcal/mole	57,9	46,1	36,1	103	88	71

VI-3- Ionisation enthalpy (ΔH_i, E_i) :

Ionisation enthalpy corresponds to the energy required to ionise a gaseous atom (convert a gaseous atom into a gaseous cation; a gaseous atom loses electrons).