Atomes et molécules

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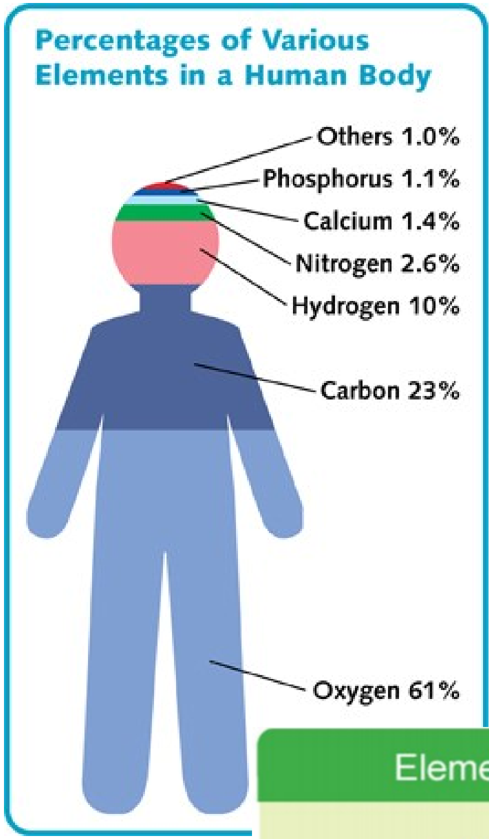
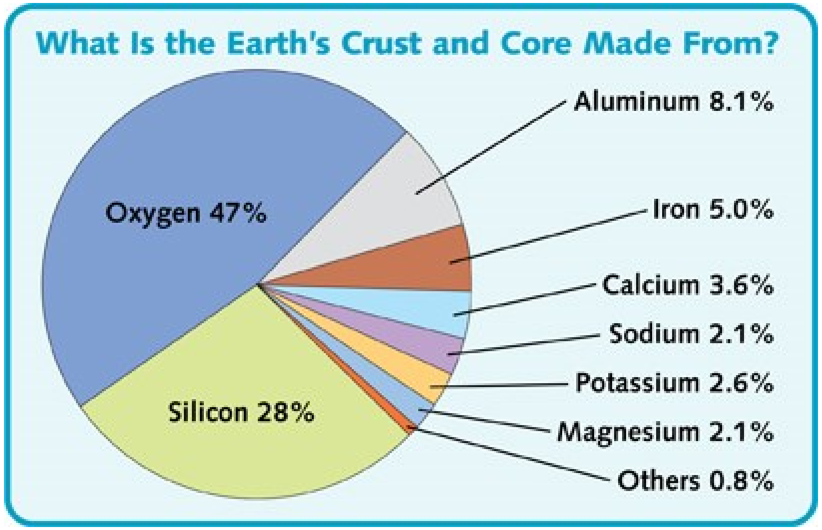
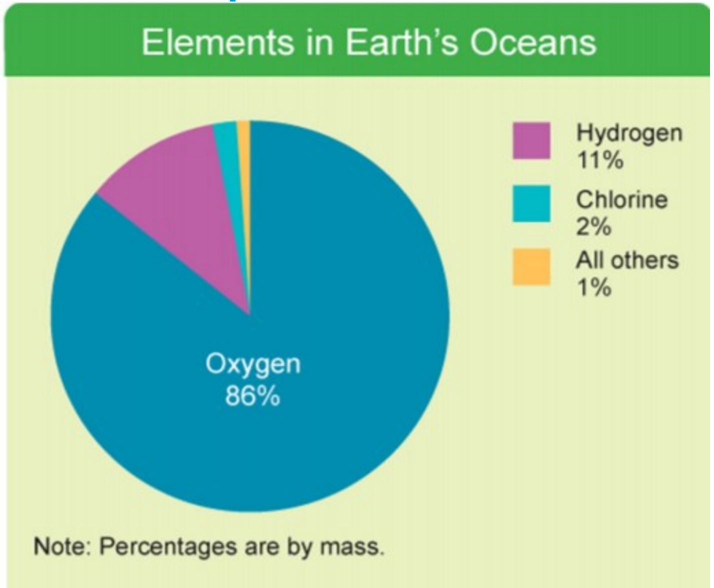
2019-2020

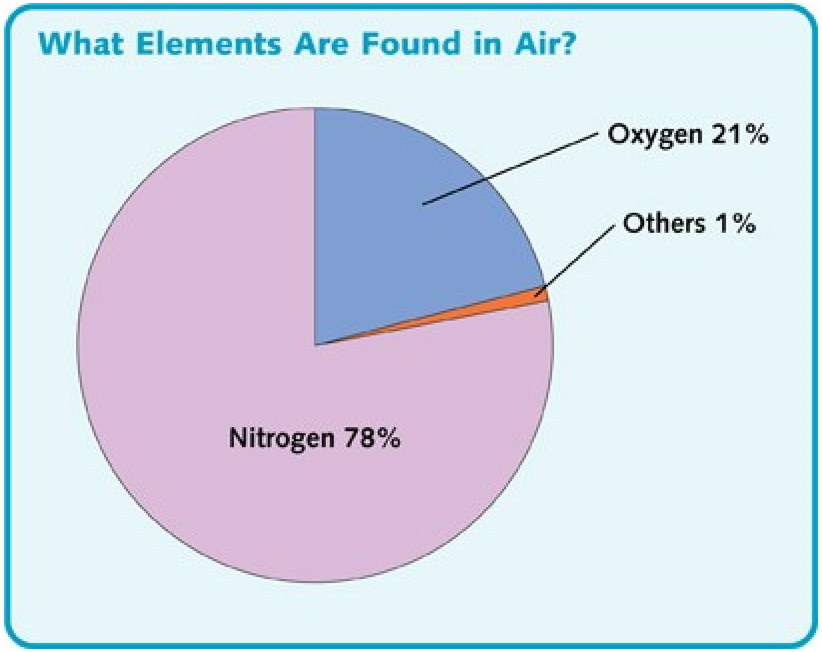
Chapter 6 : The Lewis chemical bond model

Chapter 6 – 1. Definition









Chapter 6 – Index

Chapter 6 – 1. Definition

At room temperature on earth, only a few atoms exist as isolated atoms (He, Ne, Ar, Kr, Xe)

Generally, atoms associate to form more or less complex structure.

- Molecules, made of 2 up to 1000 atoms
(examples : HCl, CH_4, amino acids, proteins etc..)

- Solid structure of atoms and ions
(examples : graphite, diamond, metals….)

Diamonds *have of strong* ***covalent bonds (Chap. 6)****, which makes it hard, but* ***Graphite*** *on the other hand has carbon atoms held by* ***weak van der Waal's bonds (Chap. 9)****.*

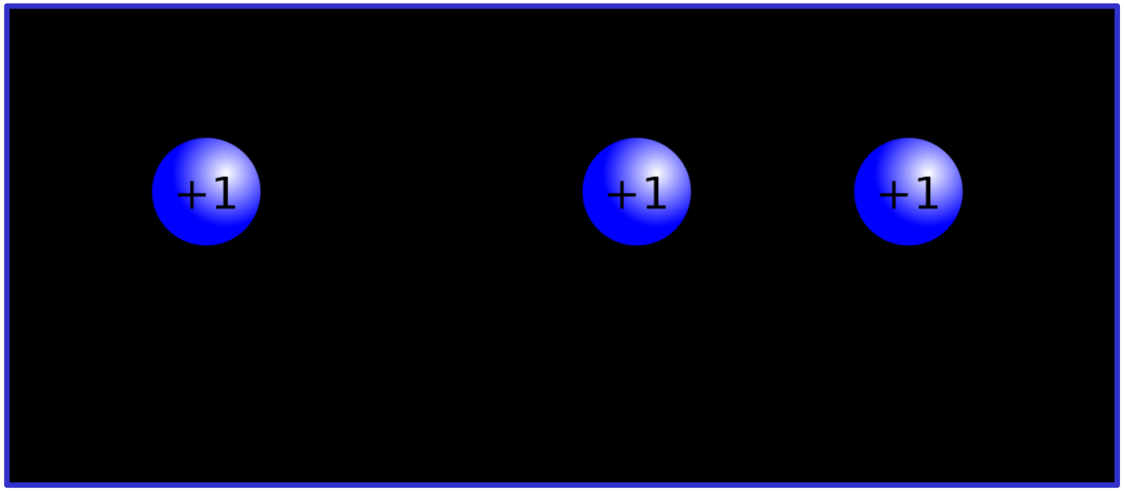
In all simple gaseous (H_2…), solid (graphite …) or liquid (Br_2…) bodies and all composed bodies (H_2O, NaCl, CH_4…), atoms are associated by chemical bonds.

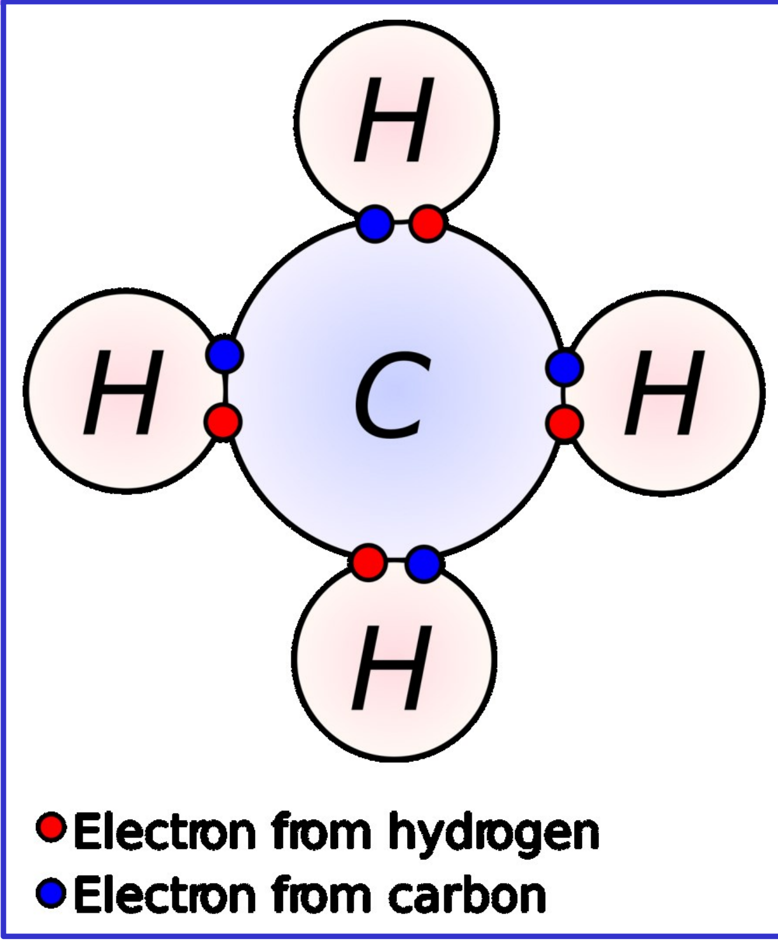
These bonds are responsible for the stability of the molecules.

Depending on the nature of the atoms, different types of chemical bonds exist.

For all types of bonds, valence electrons are responsible for the cohesion of multi-atomic structure.

2-1) Covalent bond



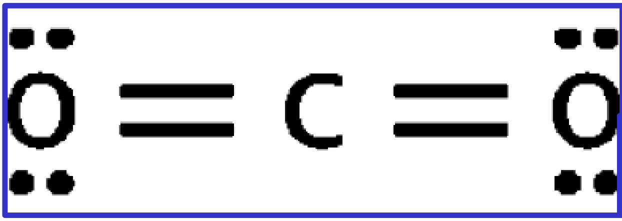


LEWIS model(1916):

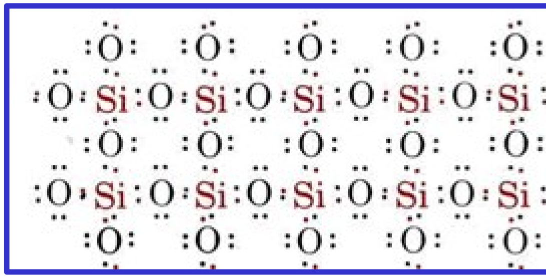
- **A covalent bond between atom A and B results from sharing a pair of electrons.**
- **Only valence electrons can participate to the bond**
- **Most of the time (but not always), atoms participating to the bond adopt the electronic configuration of the closest rare gaz (full shells).**

Covalent bonds occur between atoms belonging to close families, in particular with similar electronegativity in order to avoid charge transfer. Electrons need to be shared, not transferred

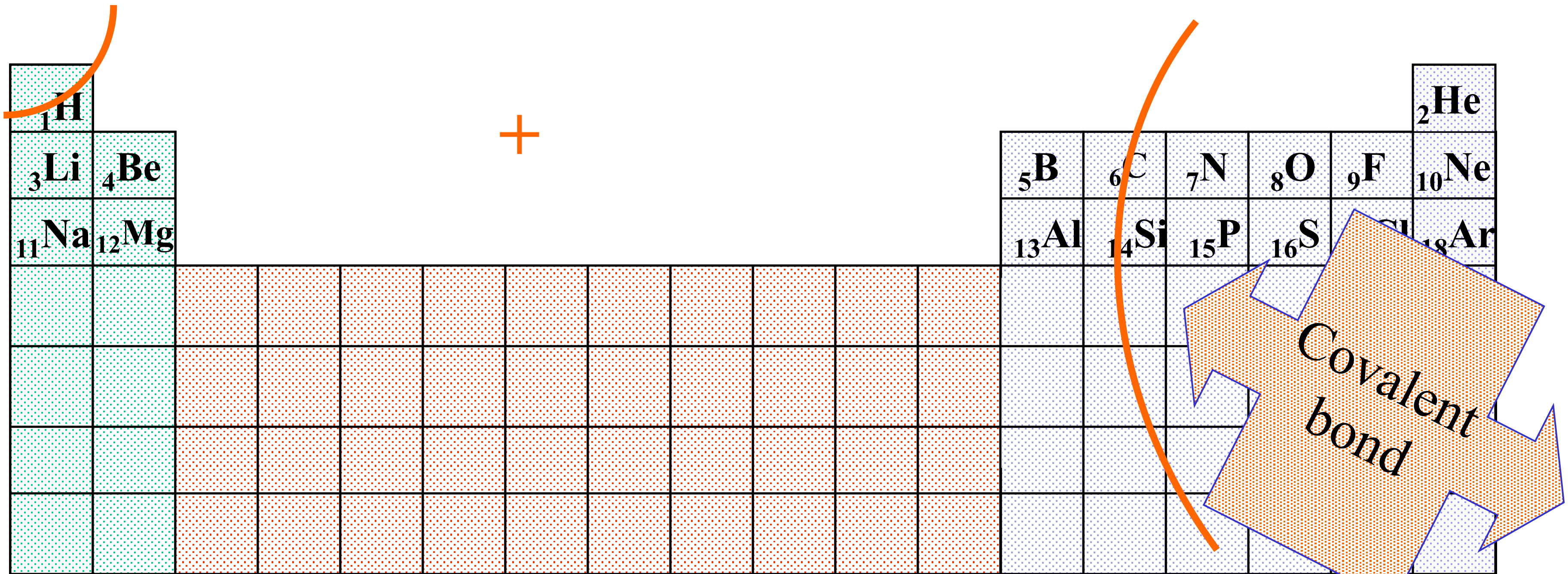
This mechanism implies that each atom must hold at least half of the electrons compared to the closest rare gas (**1 for H and 4 for the other elements**).



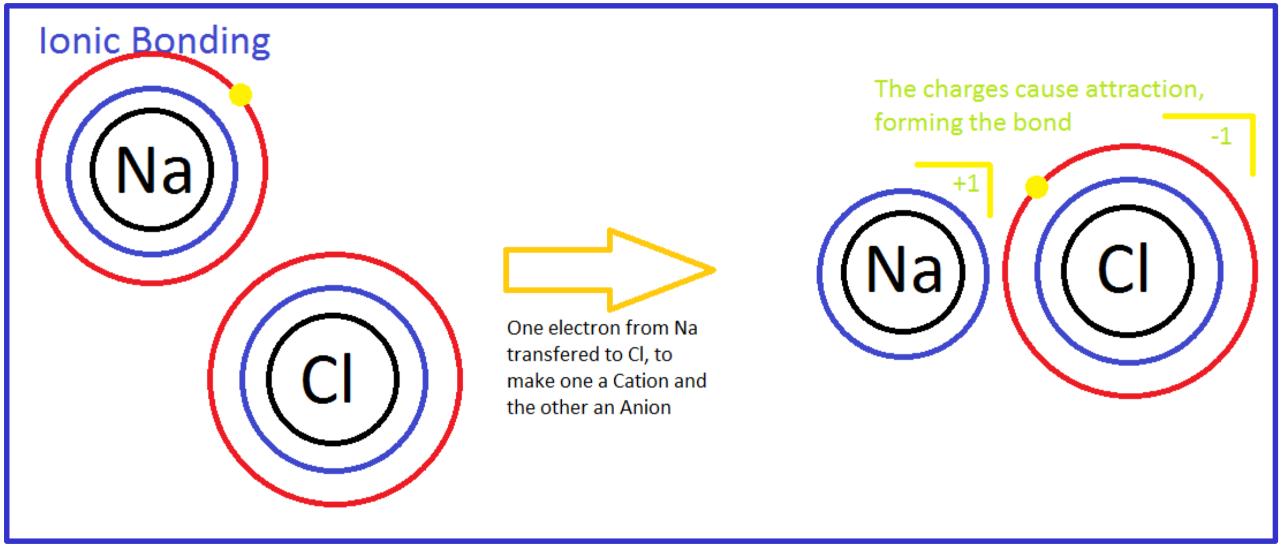
CO_2 gas



SiO_2 quartz macromolecule



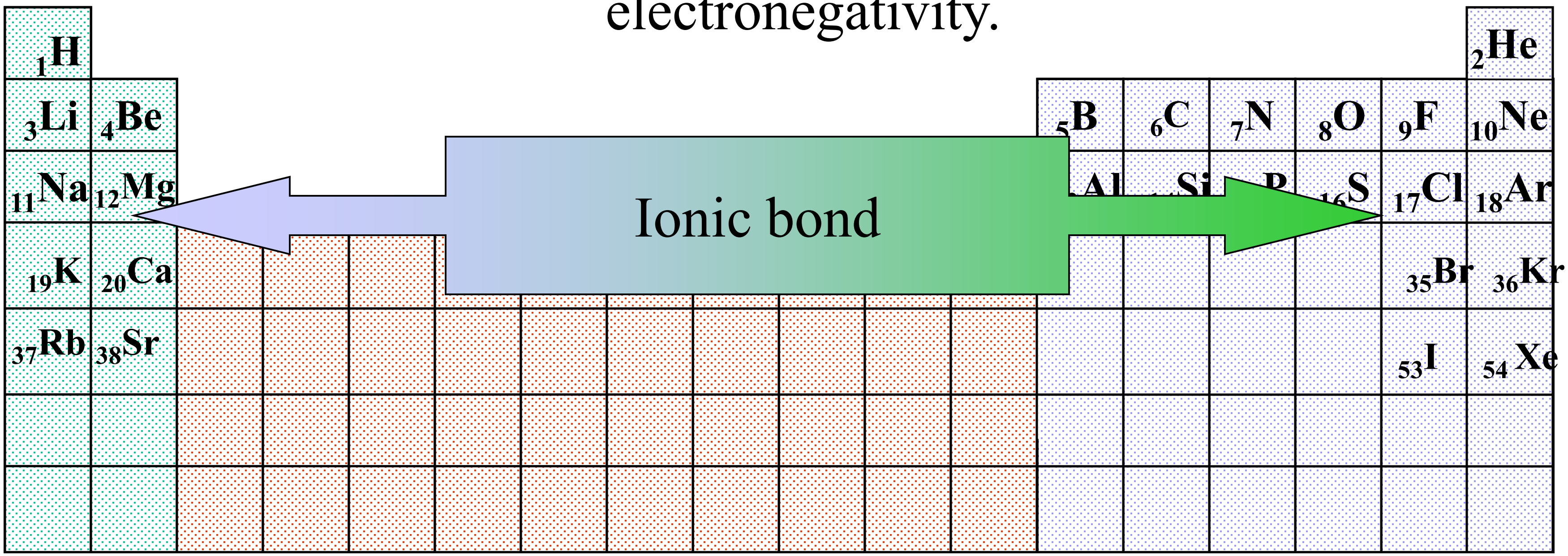
2-2) Ionic bond



- In the ionic bond , the electron is completely transferred from one atom to the other.
- One atom gives away a valence electron to the other atom, resulting in a pair of electrons localized on the most electronegative atom which becomes negatively charged (Cl).
- The atom loosing an electron (Na) becomes positively charged.
- Na takes the electronic structure of the preceding rare gas
- Cl takes the electronic structure of the following rare gas .

The ionic bond between Na^+ and Cl^- is mainly electrostatic.

This kind of bonds occurs between atoms with very different electronegativity.



Exemple : NaCl : Na^+, Cl^-

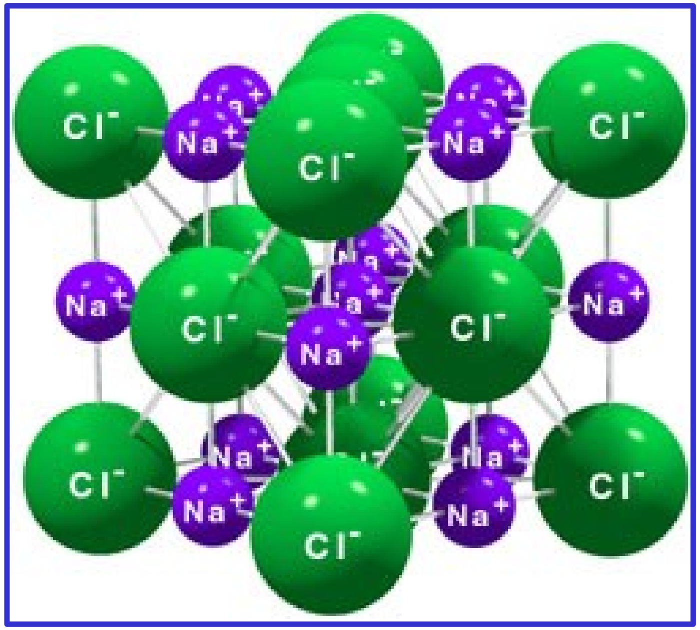
Na^+ $1s^2\ 2s^2\ 2p^6\ 3s^0$ cf Ne

Cl^- $1s^2\ 2s^2\ 2p^6\ \mathbf{3}s^2\ \mathbf{3}p^6$ cf Ar

- Ionic bonds involve electrostatic forces

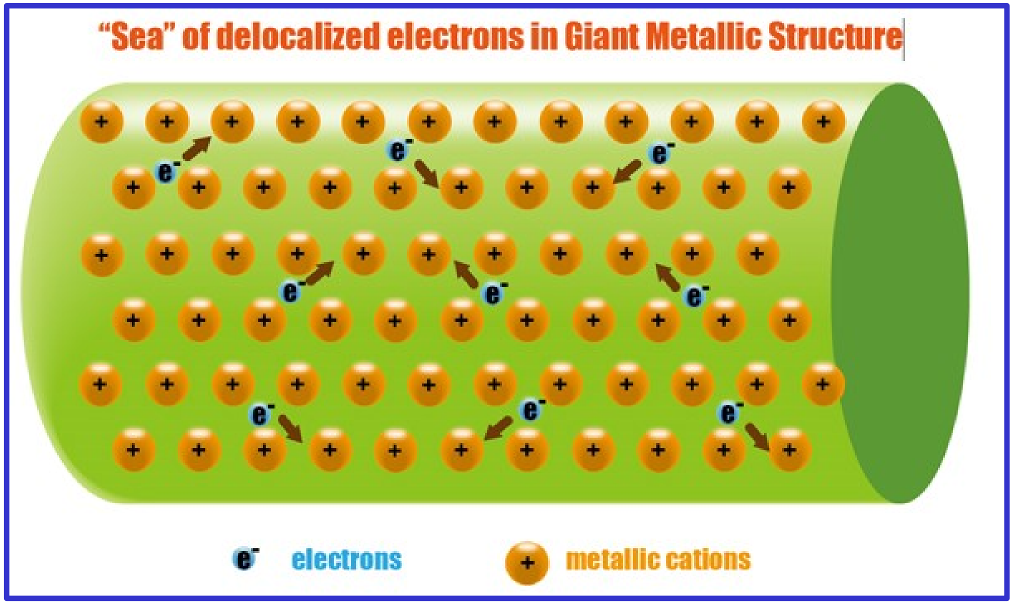
→ **Ionic bonds are strong**

- In order to break a ionic crystal, it is necessary to provide a lot of energy: (high melting temperature for NaCl: 801 °C, LiF: 845 °C),



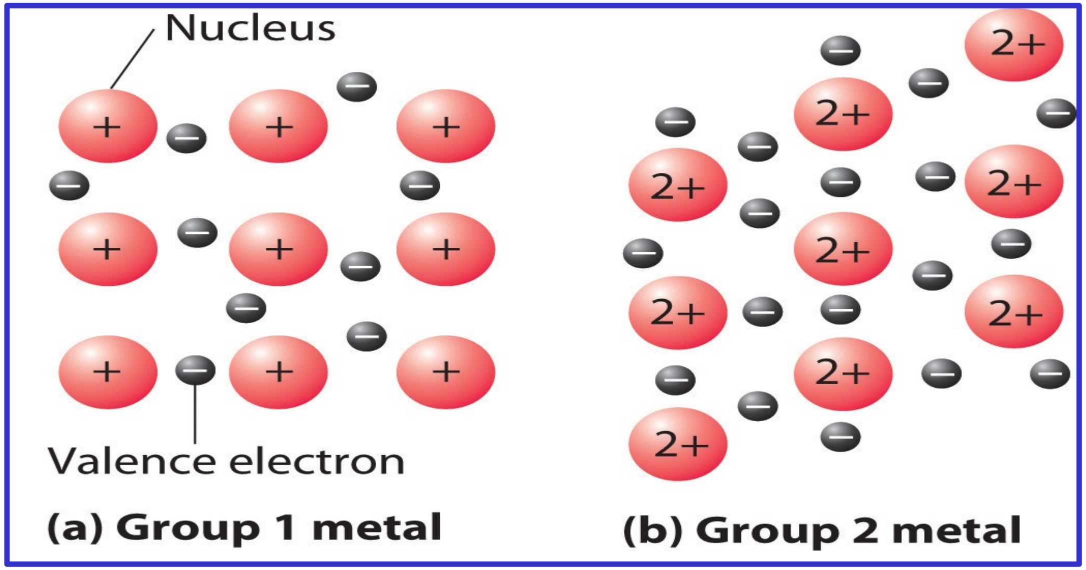
2-3) The metallic bond

- The metallic bond ensures the cohesion of purely metallic substances. Because all the atoms are the same, there can be no ionic bonding
- The strength of the metallic bond is enhanced by the sharing of all valence electrons of all atoms participating to the metallic crystal.
- Valence electrons in the metal are free to move across the whole metal surface. The metallic structure is a regular network of positive ions in a sea of free valence electrons (high conductivity).



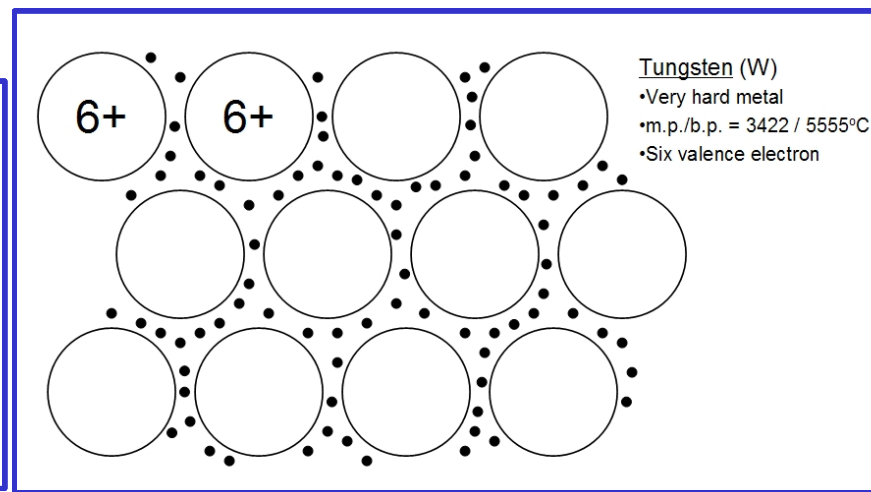
Chapter 6 – 2. Different types of bonds

Examples:



- **Transition energy from solid to gas state is of the order of 100 kJ/mole for alkali metals and alkali earth metals.**
- **Higher values (up to 800 kJ/mole)for transition metals.**

Tungsten (Wolfram), $_{74}$**W** (the highest melting point of all the elements: 3695 K)
Electronic configuration :
[Xe] **4f^{14} 5d^{4} 6s^{2}**



Periodic Table of the Elements

Xford LABS

atomic number — atomic weight

14 28.09 **Si** Silicon

symbol:

name

black solid

blue liquid

red gas

white synthetically prepared

most stable isotope

- alkali metals
- alkaline earth metals
- transitional metals
- other metals
- nonmetals
- noble gases

1 1.01 H Hydrogen																	2 4.003 He Helium
3 6.94 Li Lithium	4 9.01 Be Beryllium											5 10.81 B Boron	6 12.01 C Carbon	7 14.01 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.18 Ne Neon
11 22.99 Na Sodium	12 24.31 Mg Magnesium											13 26.98 Al Aluminum	14 28.09 Si Silicon	15 30.97 P Phosphorus	16 32.06 S Sulfur	17 35.45 Cl Chlorine	18 39.95 Ar Argon
19 39.10 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel	29 63.55 Cu Copper	30 65.37 Zn Zinc	31 69.72 Ga Gallium	32 72.59 Ge Germanium	33 74.92 As Arsenic	34 78.96 Se Selenium	35 79.90 Br Bromine	36 83.80 Kr Krypton
37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.40 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.69 Sn Tin	51 121.75 Sb Antimony	52 127.60 Te Tellurium	53 126.90 I Iodine	54 131.30 Xe Xenon
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 186.21 Re Rhenium	76 190.20 Os Osmium	77 192.22 Ir Iridium	78 195.09 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.19 Pb Lead	83 208.98 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astatine	86 (222) Rn Radon
87 (223) Fr Francium	88 226.03 Ra Radium	89 227.03 Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Ha Hahnium	106 (266) Sg Seaborgium	107 (262) Bh Bohrium	108 (265) Hs Hassium	109 (266) Mt Meitnerium	110 (271)	111 (272)	112 (277)	(113)	114 (285)	(115)	116 (289)	(117)	118 (293)
			58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 (145) Pm Promethium	62 150.40 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium	
			90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (260) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium	

- Metals are characterized by their ability to reflect light, their high electrical and thermal conductivity, their high heat capacity, and their malleability. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.
- Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.
- Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W).

QCM 13 Dans le modèle de la liaison ionique :

a. il y a transfert d'électron(s) de l'élément le plus électronégatif vers l'élément le moins électronégatif

b. il y a transfert d'électron(s) de l'élément le moins électronégatif vers l'élément le plus électronégatif

c. il y a transfert d'électron(s) de l'élément possédant le rayon atomique le plus grand vers l'élément possédant le rayon atomique le plus petit

d. il y a transfert d'électron(s) de l'élément possédant le rayon atomique le plus petit vers l'élément possédant le rayon atomique le plus grand

e. Aucune des propositions précédentes (A à D) n'est exacte

3) Covalent Lewis model

- pure covalent bonds, dative bonds and multiple bonds.
- Different models have been elaborated concerning the formation of bonds.

1. **Lewis model**
2. Quantum model

3-1) The covalent bond

Each atom provides a single valence electron and contributes to forming an electron pair shared by both atoms (ex: H_2).

In the case of molecules and simple ions, the **LEWIS STRUCTURE** can be established.

- from the LEWIS structure of atoms
- from the quantum cell representation of the valence shells.

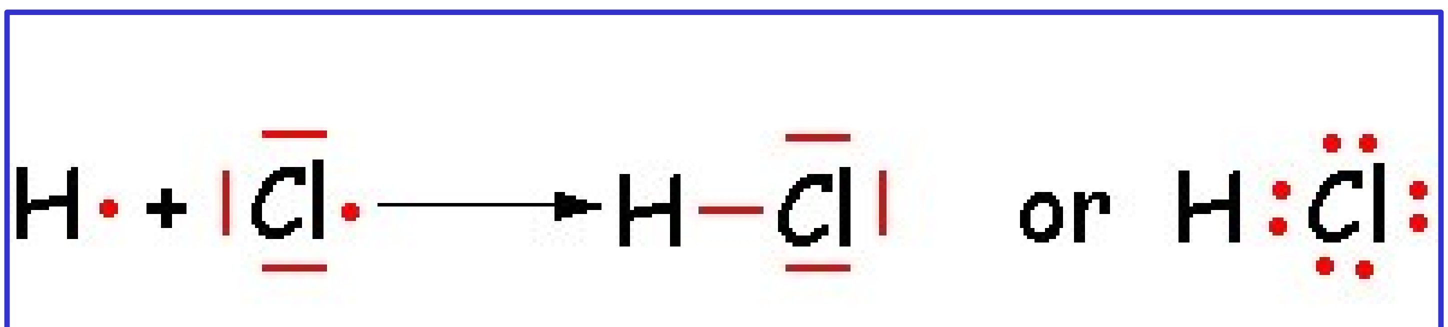
Chapter 6 – 3. Covalent Lewis model

Lewis structures are symbolic representations:

- All electrons from the external shells must be represented whether they are involved in the bond or not.

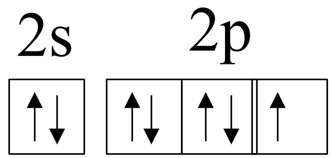
- A pair of electrons **involved** in the bond is called a bonding pair.
- A pair of electrons **NOT involved** in a bond is called a lone pair.

Bonding pairs and lone pairs are represented by segments (or double dots)

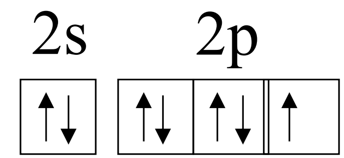


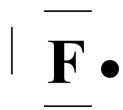
Example 1 : F_2

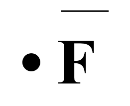
$_9F$ $1s^2\ 2s^2\ 2p^5$



Valence shell
(n = 2)



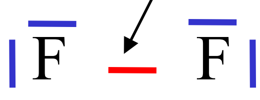




Sharing their single electrons

≡ Covalent bond

≡ **Bonding pair** of electrons belonging to both atoms



3 lone pairs

3 lone pairs

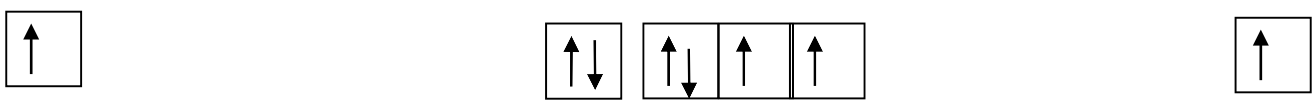
Example 2 : H_2O

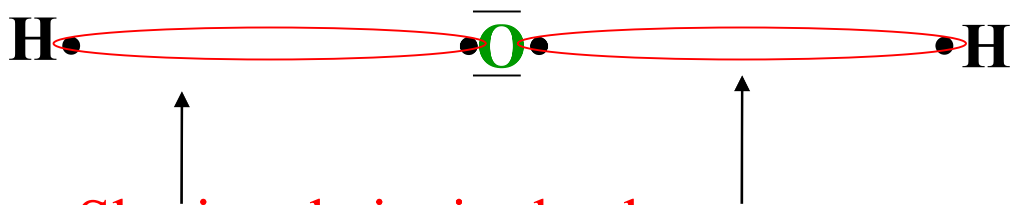
Oxygen atom associated with 2 Hydrogen atoms.

${}_{1}H$ $1s^1$ — Valence shell (n = 1)

${}_{8}O$ $1s^2\ \underbrace{2s^2\ 2p^4}$ — Valence shell (n = 2)

${}_{1}H$ $1s^1$ — Valence shell (n = 1)

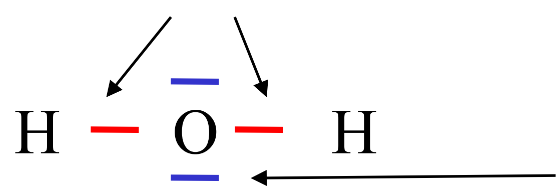




Sharing their single electrons

≡ Covalent bond

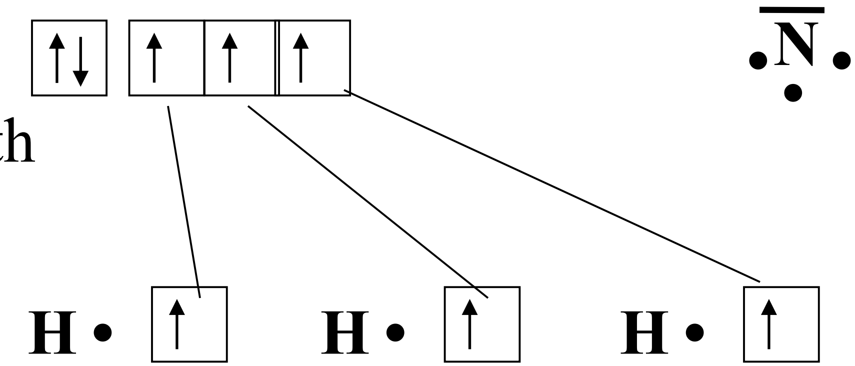
≡ **Bonding pairs** of electrons belonging to both atoms



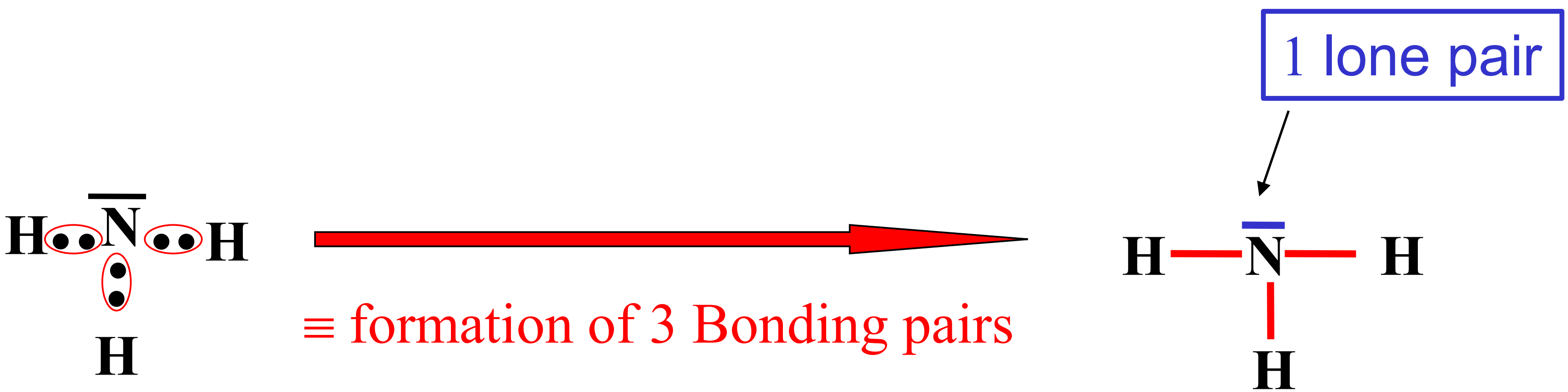
2 lone pairs of electrons on the Oxygen atom

Exemple 3 : NH_3 $\quad {}_7N \quad 1s^2\ 2s^2\ 2p^3$

Valence shell (n = 2)



The nitrogen atom associates with 3 Hydrogen atoms to form the **ammonia molecule**?

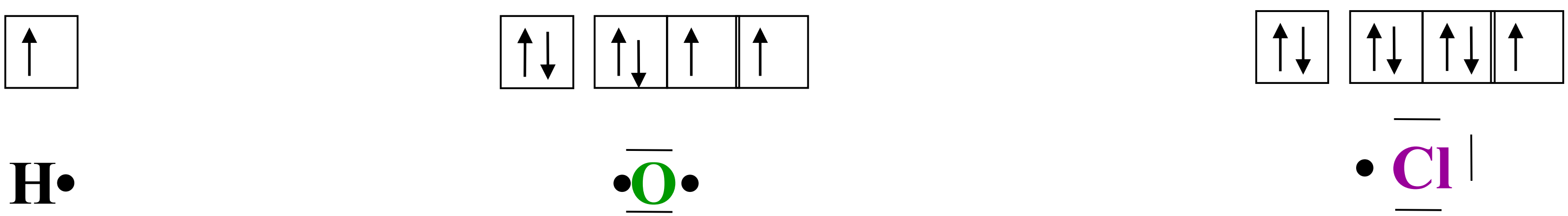


Exemple 4 : HOCl (Hypochlorous acid)

$_{1}H$ $1s^1$

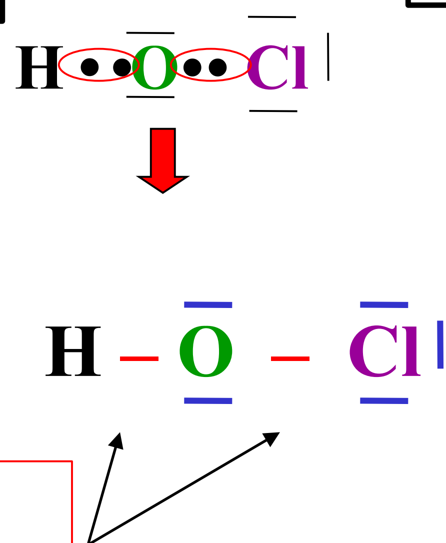
$_{8}O$ $1s^2\ \underbrace{2s^2\ 2p^4}_{\text{Valence shell } (n = 2)}$

$_{17}Cl$ $1s^2\ 2s^2\ 2p^6\ \underbrace{3s^2\ 3p^5}_{\text{Valence shell } (n = 3)}$



Oxygen associates with hydrogen

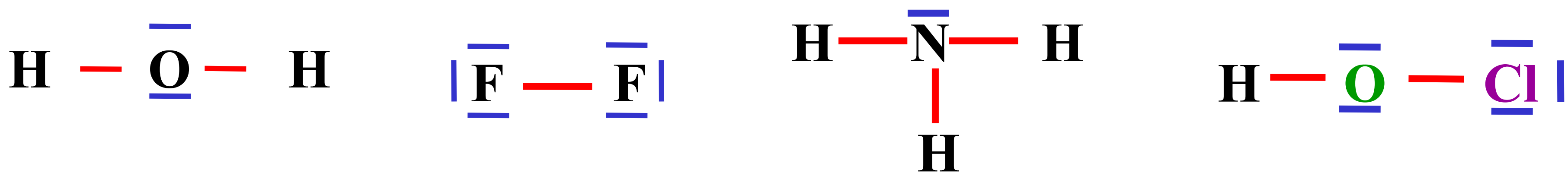
Oxygen associates with chlorine



≡ formation of 2 Bonding pairs

Hypochlorous acid is a weak acid with the chemical formula HClO. It forms when chlorine dissolves in water, and it is HClO that actually does the disinfection when chlorine is used to disinfect water for human use.

Chapter 6 – 3. Covalent Lewis model



In the examples above, each hydrogen atom is surrounded by 2 electrons. The other atoms are surronded by 8 electrons.

This is the OCTET RULE:

When forming bonds, atoms tend to saturate their valence shell in order to get the **electronic structure of the closest rare gas**.

With the exception of Hydrogen, all atoms involved in covalent bonding are surrounded by 8 electrons.

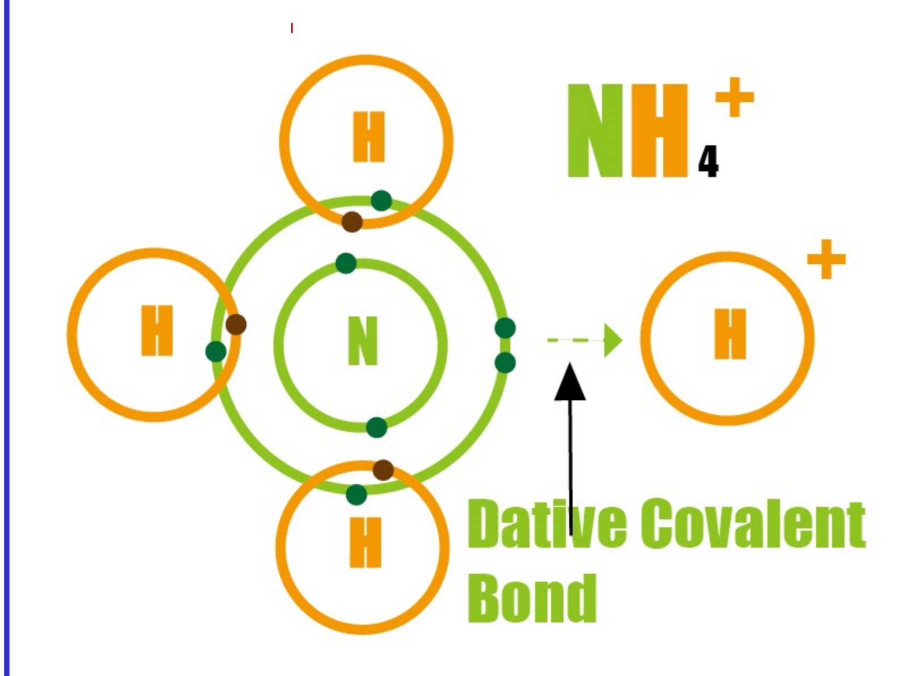
………But there are many exceptions to the rule!!!

3-2) Dipolar or dative covalent bond

A $\square$ + B | $\longrightarrow$ A $\longleftarrow$ B

Here, atom B has a lone pair and brings both electrons to form the covalent bond. This is possible for 2 atoms when one atom has a lone pair and the other atom has an electron vacancy.

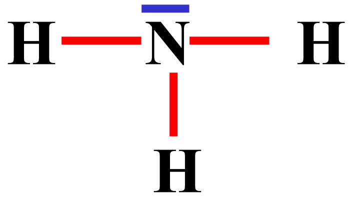
This kind of bond is strictly covalent : only the formation of the bond is different. Once formed it is similar to any covalent bond, but in the LEWIS representation it is represented by an arrow representing the bonding pair



B is called a Lewis base ; A is a Lewis acid

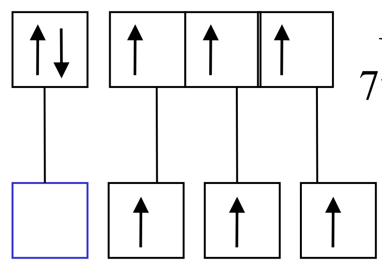
Example : formation of the ammonium ion NH_4^+

NH_3

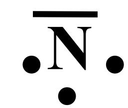


Nitrogen has one lone pair; a dative bond is possible.

H+ has an electron vacancy

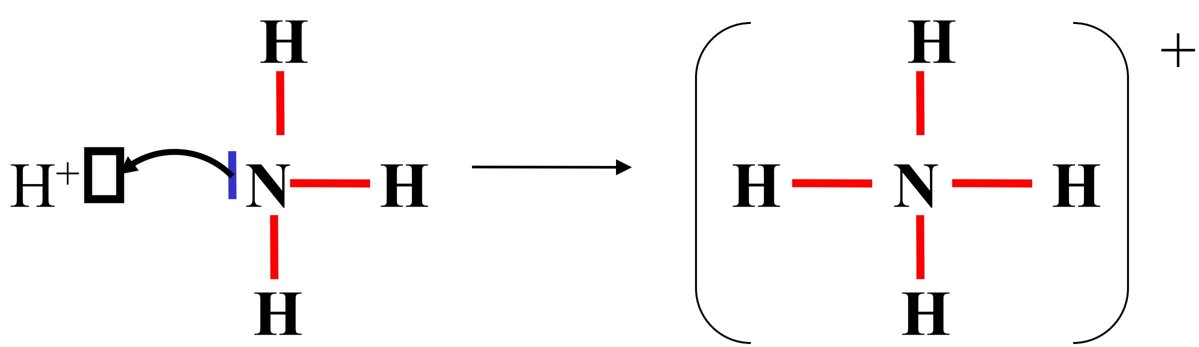


$_7N$ $\underbrace{1s^2 \, 2s^2 \, 2p^3}$



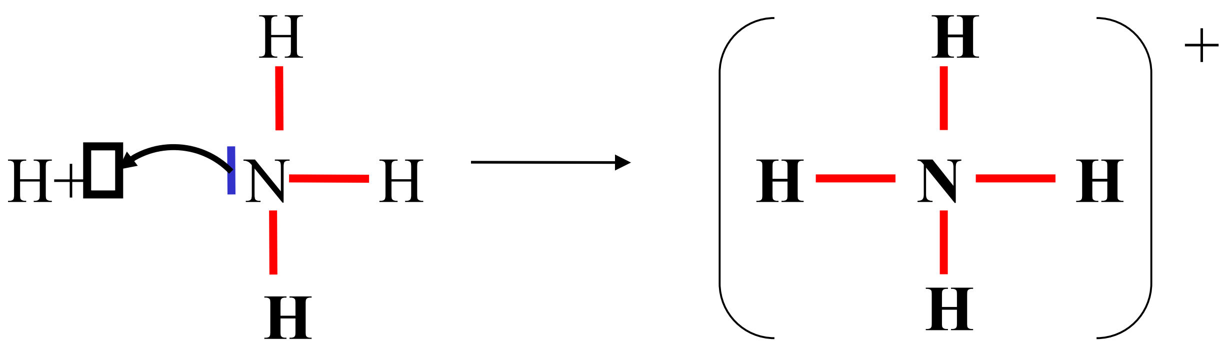
H^+ $1s^0$

3 x H $1s^1$



All 4 bonds N - H are finally equivalent

Formal charges



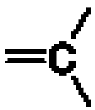
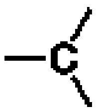
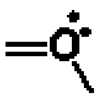
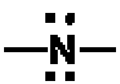
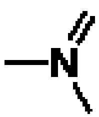
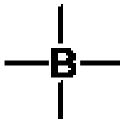
- One proton in excess compared to the number of electrons: the positive charge is assigned to the whole molecule
- Nitrogen is an electron provider: the lone pair of nitrogen is now shared with the hydrogen. Nitrogen has « lost » half of the pair, **formally one electron charge (+1)**.
- The H^+ has won a negative charge and **has became neutral (0)**.

Assuming that electrons are shared equally in a bond regardless of electronegativity, **the formal charge is**:

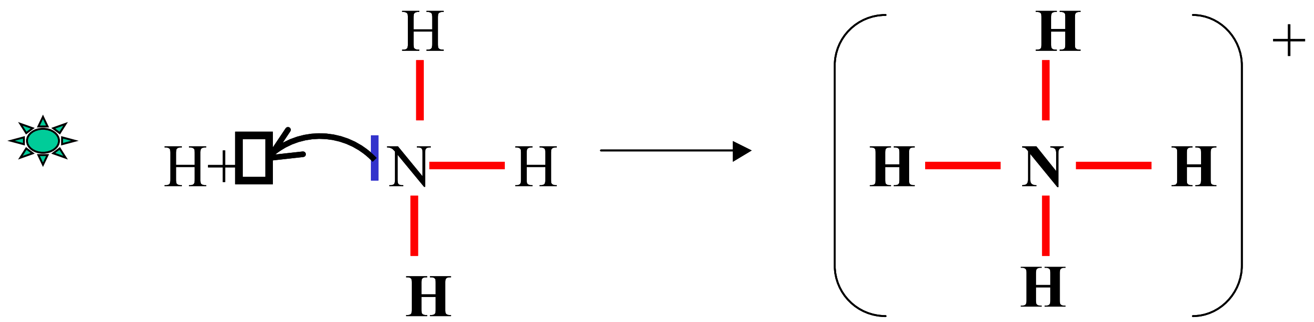
Formal Charge = (valence number) - (number of bonds) - (non-bonding electrons)

Chapter 6 – 3. Covalent Lewis model

Formal Charge = (valence number) - (number of bonds) - (non-bonding electrons)

Atom	Valence #	-	# bonds	-	nonbonded e's	=	Formal Charge
	4	-	4	-	0	=	0
	4	-	3	-	0	=	+1
	6	-	3	-	2	=	+1
	5	-	2	-	4	=	-1
	5	-	4	-	0	=	+1
	3	-	4	-	0	=	-1

Example : calculating the formal charge for nitrogen in NH_4^+



- Nitrogen has 5 valence electrons.
- In NH_4^+, nitrogen builds 4 bonds
- Nitrogen has 0 non bonding electrons

Formal Charge (N) = (valence number) - (number of bonds) - (non-bonding electrons)

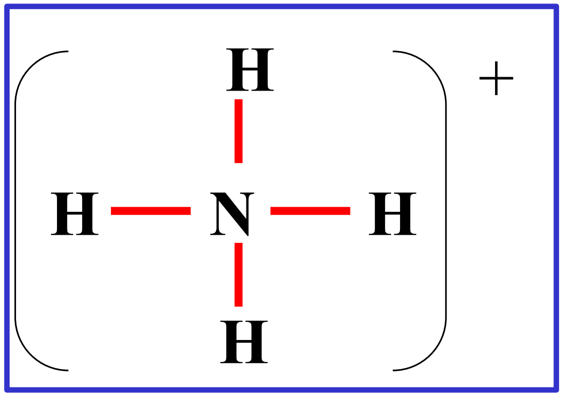
= $5 - 4 = +1$

In this molecule, **nitrogen has a formal charge of +1**
On the other hand all **H atoms have a formal charge of 0**.

Formal Charge (H) = (valence number) - (number of bonds) - (non-bonding electrons)

= $1 - 1 = 0$

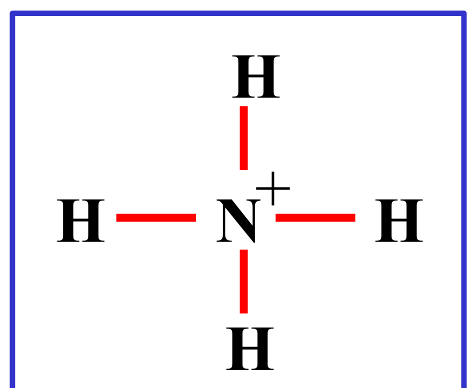
The sum of all the formal charges of all the atoms is equal to the global charge. **0 for all neutral molecules**. Positive or negative values depending on the charge for ions.



Ammonium ion:
FC (N) + 4 [FC (H]) = +1 + 4(0) = +1

In the case of ammonium, the positive value corresponds to the loss of electron by the nitrogen.

The positive charge is indicated on N:

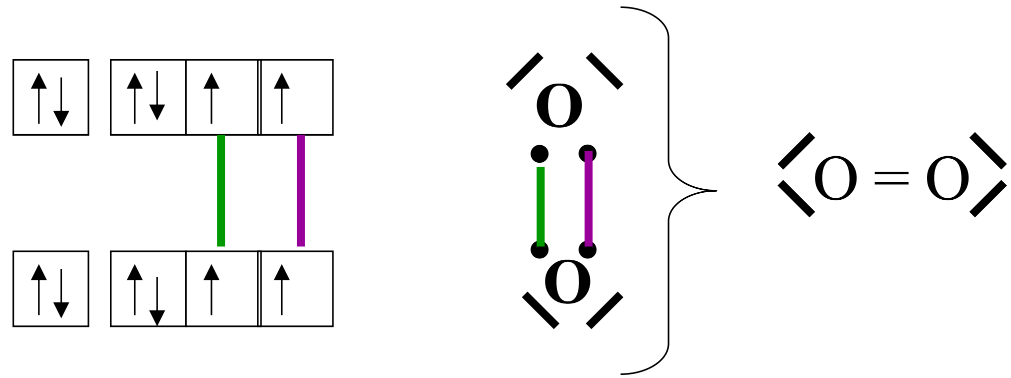


3-3) Multiple bonds: Double and triple bonds

Example 1: O_2 molecule

$_{8}O$ $1s^2\ \underbrace{2s^2\ 2p^4}$

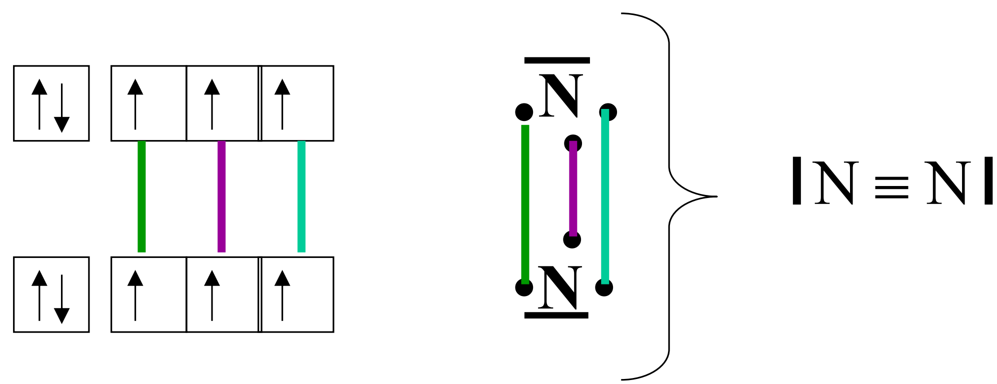
$_{8}O$ $1s^2\ \underbrace{2s^2\ 2p^4}$



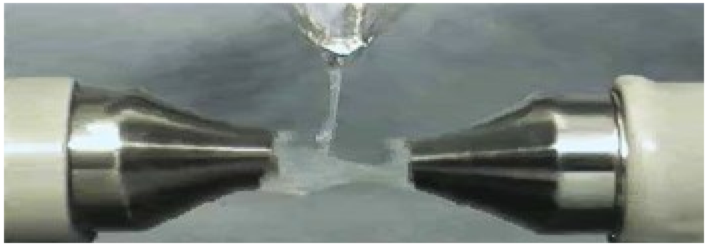
Example 2 : N_2 molecule

$_{7}N$ $1s^2\ \underbrace{2s^2\ 2p^3}$

$_{7}N$ $1s^2\ \underbrace{2s^2\ 2p^3}$



O_2 is paramagnetic (and not N_2) !!



- Being **paramagnetic means** having **unpaired electrons** and the individual magnetic effects **do** not cancel each other out. The unpaired electrons carry a magnetic moment that gets stronger with the number of unpaired electrons causing the atom or ion to be attracted to an external magnetic field.
- **Note that according to the Lewis model O_2 has no unpaired electrons but according to Molecular Orbital (MO) theory it does have unpaired electrons. Since liquid O_2 does stick to a magnet, MO theory is better at explaining the behavior.**

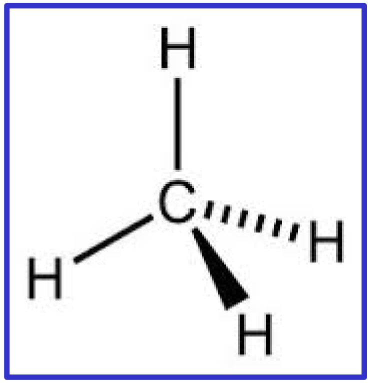
3-4) Valence states

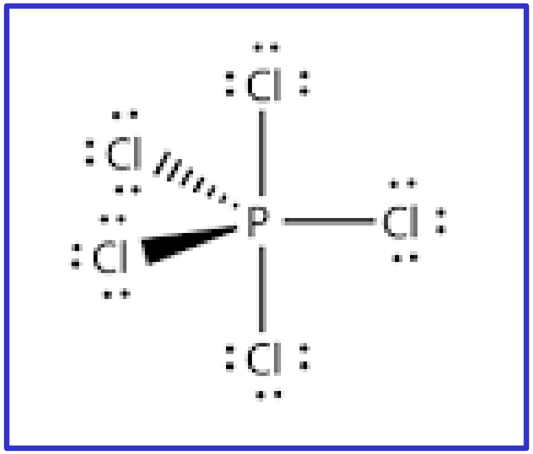
- In some cases it is necessary to invoke a **valence state** of the atom to account for some molecules.

⟺ First case: increasing the number of lone electrons

Examples:

- Methane CH_4 (**verifying the OCTET RULE**)
- Phosphorus pentachloride PCl_5 (**NOT verifying the OCTET RULE**)



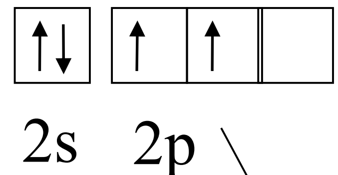


Chapter 6 – 3. Covalent Lewis model

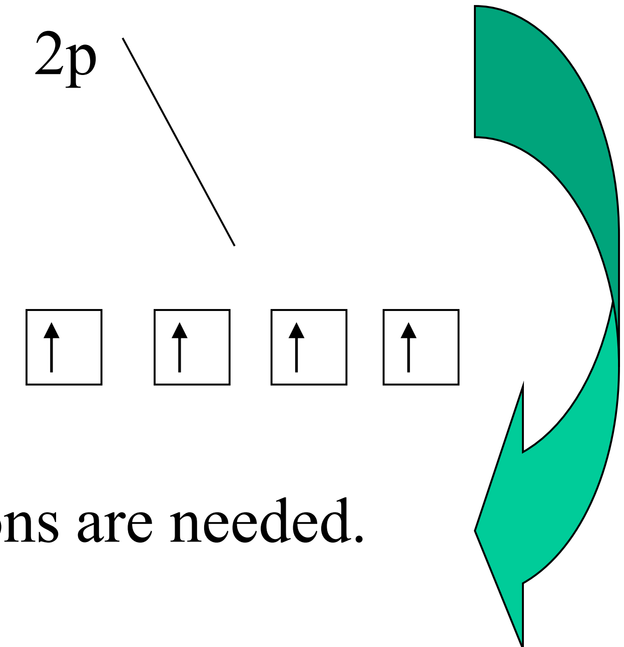
Electronic configuration of carbon in the fundamental state:

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

Valence shell (n = 2)



4 bonds with hydrogen?



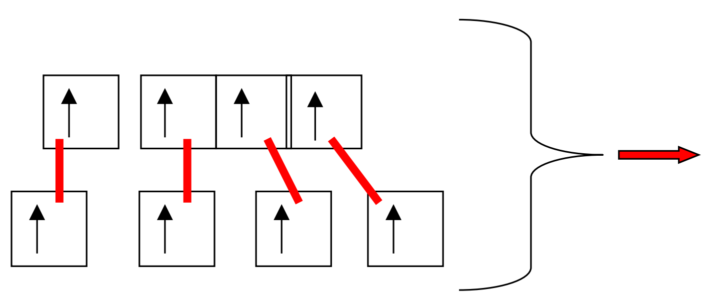
$_1H$ $1s^1$ **H•**

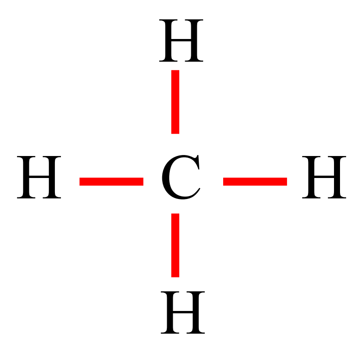
In order to form 4 C-H bonds, 4 single electrons are needed.

Here the carbon is in a valence state, maximizing the number of single electrons.

C*

4 x H



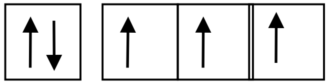


Chapter 6 – 3. Covalent Lewis model

Electronic configuration of phosphorus in the fundamental state:

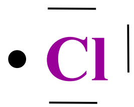
$_{15}P$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

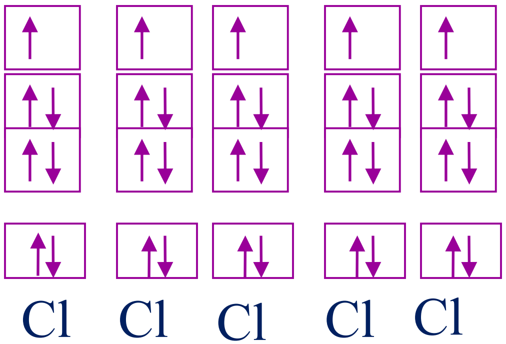
Valence shell (n = 3)



5 bonds with chlorine atoms ?

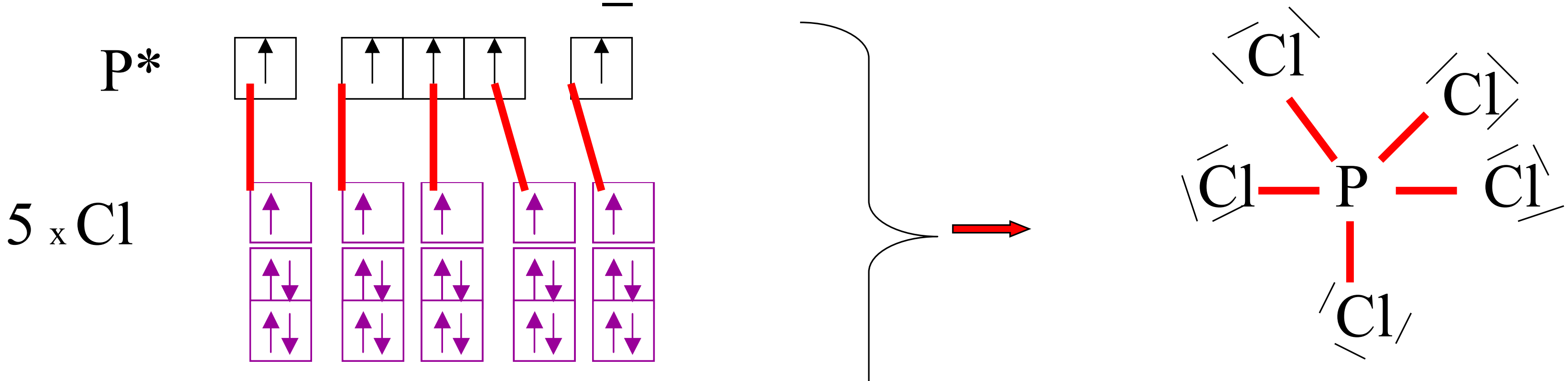
$_{17}Cl$ $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^5$





In order to form 5 P-Cl bonds, 5 single electrons are needed

<u>The valence state of P in PCl_5 is</u> :



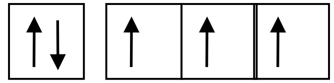
(≠ Règle de l'octet)

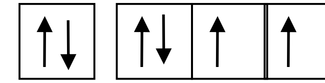
⟺ Second case: creating empty orbitals

Instead of maximizing the number of single electrons, it can be necessary to create additionaly lone pairs in order to create empty quantum cells

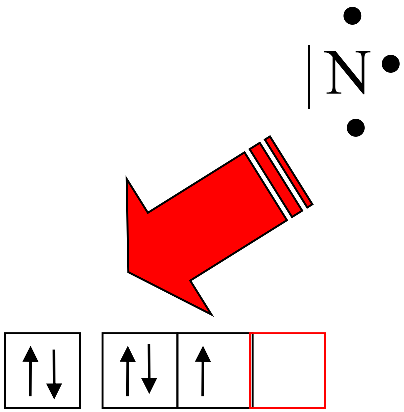
Exemple : N_2O (SO_2) …

N_2O : N is connected to another N and to O

$_7N$ $1s^2\ 2s^2\ 2p^3$ 

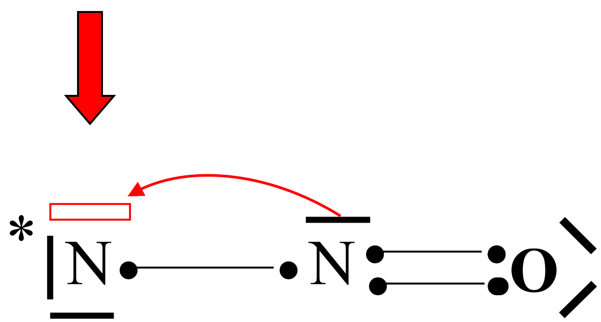
$_8O$ $1s^2\ 2s^2\ 2p^4$ 

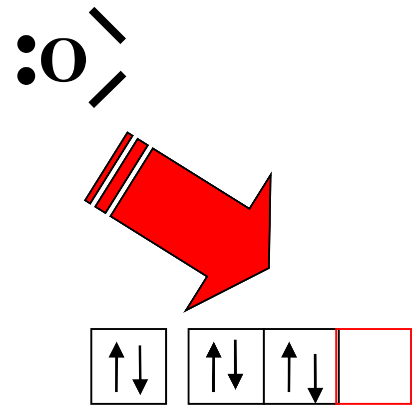
Two possibilities



Creation of an empty cell for N

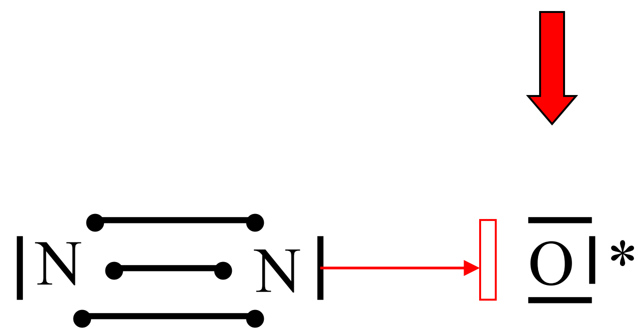
≡ Valence state N*



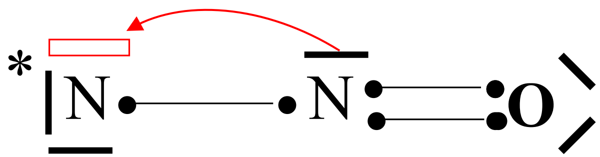


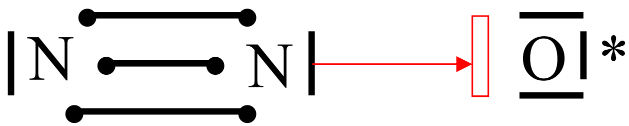
Creation of an empty cell for O

≡ Valence state O*



An empty cell can be created in the valence shell of nitrogen or oxygen: different Lewis structures are possible :



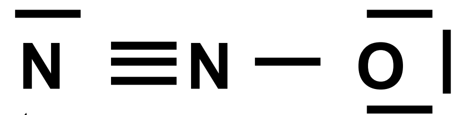


A

CF = 5 – 6 = -1

CF = 5 – 4 = +1

CF = 6 – 6 = 0



B

CF = 5 – 5 = 0

CF = 5 – 4 = +1

CF = 6 – 7 = -1

Formal Charge = (valence number) - (number of bonds) - (non-bonding electrons)

3- 5) Mesomerism or resonance

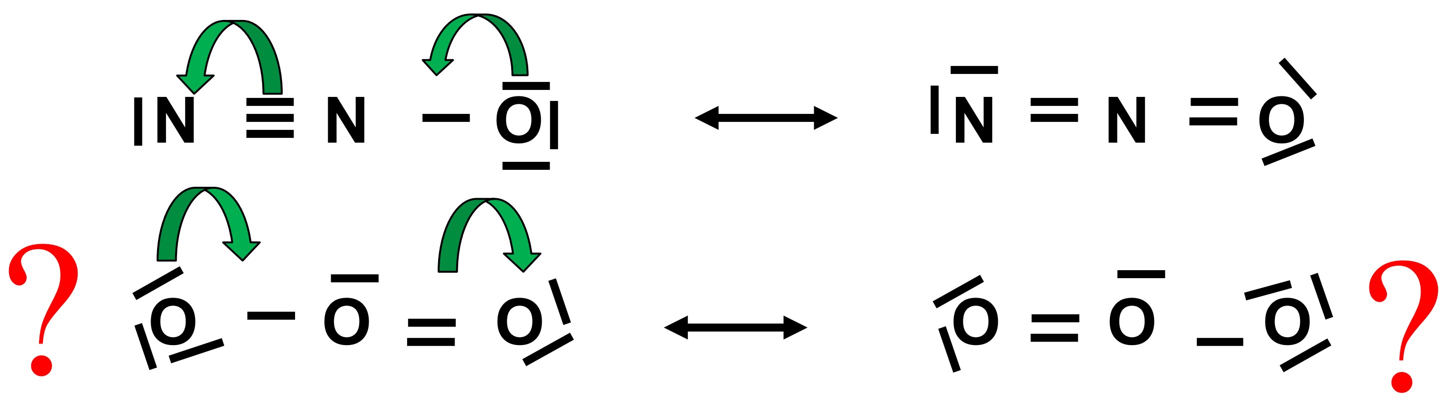
The structures A and B differ only by the positions of lone pairs

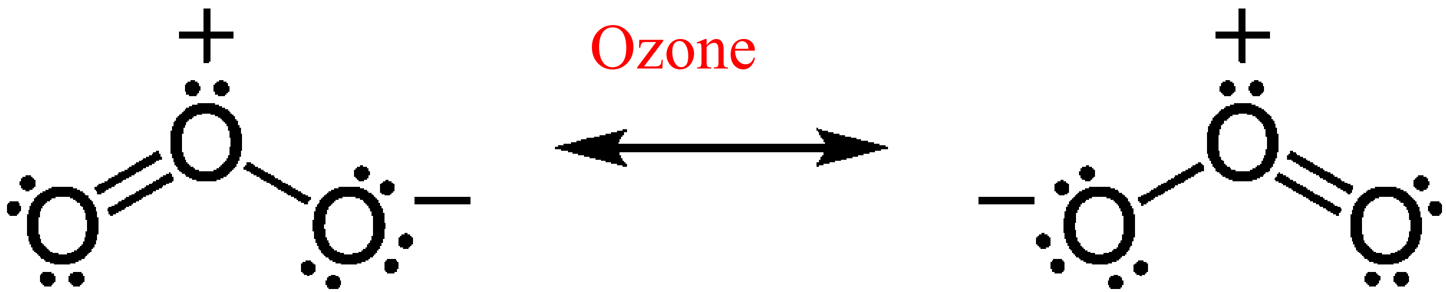
This is called delocalization of electrons

The real structure cannot be represented by a single structure. It is called a **<u>HYBRID</u>** of structure A and B.

Both structure A and B are:

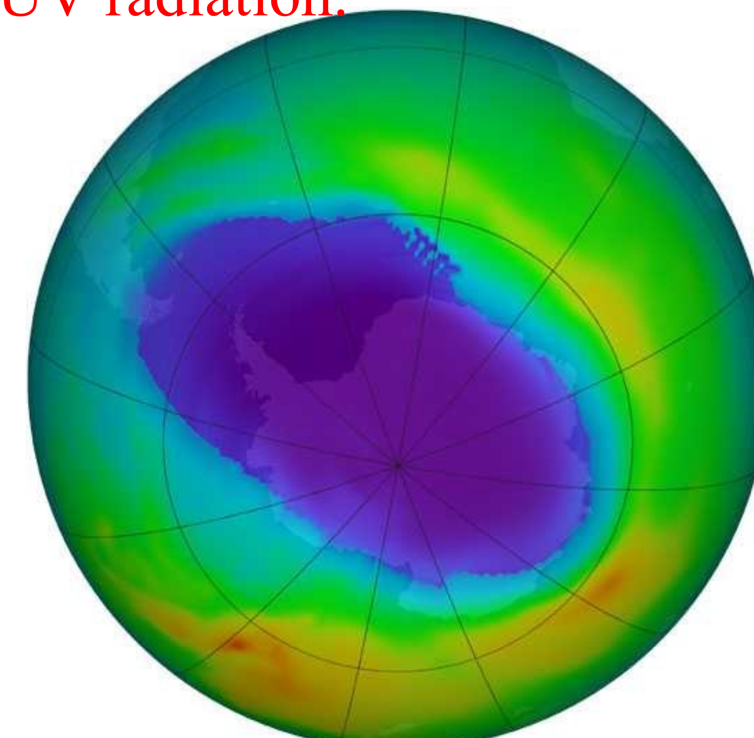
Resonance or mesomeric structure

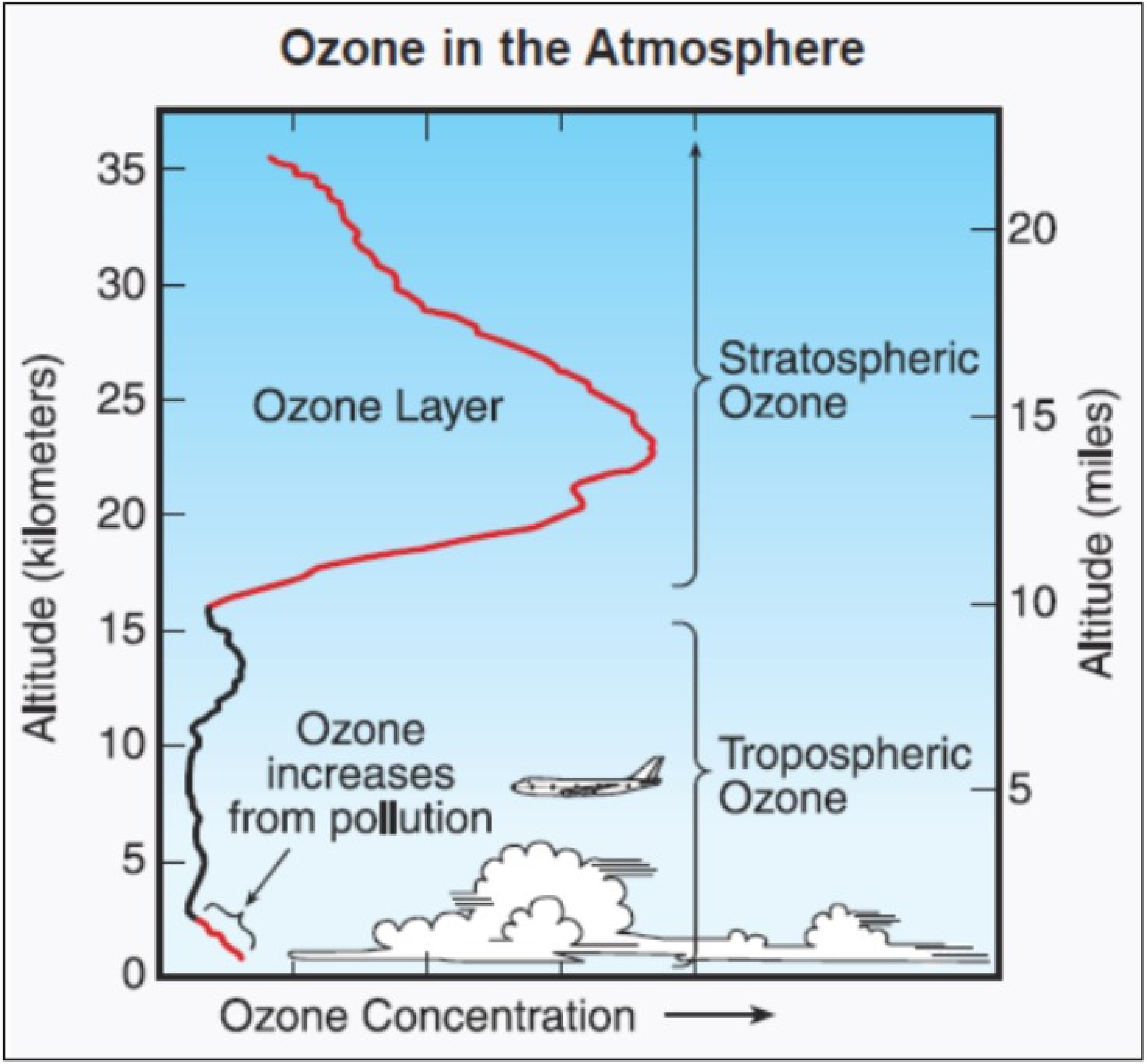




Ozone is toxic for humans at a certain level in the troposphere.

The Ozone hole is observed at the altitude of 25 km in the stratosphere. It is protecting living organism from strong UV radiation.





Ozone in the Atmosphere
Altitude (kilometers)
35
30
25
20
15
10
5
0
Ozone Layer
Ozone
increases
from pollution
Stratospheric
Ozone
Tropospheric
Ozone
20
15
10
5
Altitude (miles)
Ozone Concentration

3-6) Bond energy

- The bond energy E_l corresponds to the energy (negative value) used to form the bond from the initial isolated atoms
- The absolute value $|E_l|$ corresponds to the necessary energy to break the bond? The value $|E_l|$ depends on:
  - The chemical species involved:

Example: **H- F** $\mathbf{|E_l| = 565\ kJ.mol^{-1}}$

H- I $\mathbf{|E_l| = 295\ kJ.mol^{-1}}$

  - The multiplicity of the bond:

C — C $\mathbf{|E_l| = 347\ kJ.mol^{-1}}$

C ≡ C $\mathbf{|E_l| = 837\ kJ.mol^{-1}}$

3-7) Conclusion

The Lewis structure has no physical reality. Atoms do not really "share" electrons. But Lewis structures are most of the time good symbolic representations of covalent bonds.

- **The Lewis model** allows to understand basic mechanism of formation and breaking of bonds:

- Not adapted to describe hybrid structures.

- Does not allow to understand the geometry of the molecules which is crucial to chemical and biological properties.

VSEPR theory

Quelques règles de nomenclature

1) Composés moléculaires minéraux

En général, ils sont composés de 2 non- métaux : $A_x B_y$
Le plus électronégatif est écrit à droite

- ***On commence par nommer l'élément écrit à droite***

  Si B est l'oxygène, on parle d'oxyde.
  Souvent racine du nom de l'élément B + terminaison ure

  Ex: si B = Cl , on parle de chlorure

- ***Si y > 1, on affecte le nom d'un*** **préfixe**

  Di, Tri, Tetra, Penta, Hexa etc...

  Ex: Si O_2 C'est un Dioxyde

- ***Puis on nomme l'élément écrit à gauche en l'affectant d'un*** **préfixe**

  si x > 1 Di, Tri, Tetra, Penta, Hexa etc...

Ex: PCl_5 pentachlorure de phosphore ; SF_6 hexafluorure de soufre
Si O_2 dioxyde de silicium ; N_2O monoxyde de diazote

2) Composés ioniques : écriture et nomenclature

On écrit le cation à gauche et l'anion à droite.

ex : Na^+Cl^- ; $(NH_4)^+ (NO_3)^-$

On nomme l'anion en premier, ensuite le cation.

IV-1-a) Composés ioniques binaires: $NaBr$, K_2S, $CaCl_2$, $FeCl_3$

***Nomenclature de l'anion* : Souvent, racine du nom de l'élément + terminaison URE**

$Na^+ Br^-$ BromURE

Pour S et N, racine latine + URE

SulfURE pour S

NitrURE pour N

Pour O, OXYDE

***Nomenclature du cation* : nom de l'élément. <u>Attention, certains cations peuvent exister sous des formes ioniques différentes</u>**

ex: Na^+Br^- bromure de sodium ; K_2S ($2K^+S^{2-}$) sulfure de potassium

$CaCl_2$ (Ca^{2+},$2Cl^-$) chlorure de calcium ; $FeCl_3$ (Fe^{3+},$3Cl^-$) chlorure de fer(III)

IV-1-B) Composés ioniques polyatomiques

Même principe (on nomme l'anion puis le cation)

NH_4^+	ammonium		
NO_3^-	nitrate	CN^-	cyanure
SO_4^{2-}	sulfate	SCN^-	thiocyanate
PO_4^{3-}	phosphate	H^-	hydrure
$H_2PO_4^-$	dihydrogénophosphate		
CO_3^{2-}	carbonate	HO^-	hydroxyde
HCO_3^-	hydrogénocarbonate		
ClO^-	hypochlorite		
ClO_4^-	perchlorate		
HPO_4^{2-}	hydrogénophosphate		
MnO_4^-	permanganate		