Chapter III: Periodic classification of the elements

I- Mendeleïev's classification (1869).

Initially based by Mendeleïev on the classification of elements by growing atomic mass, the modern classification is based on the classification of elements by growing atomic number Z, and is therefore based on the electronic structure of atoms (outer layer).
- It is composed of 7 rows called "periods" and 18 columns called "families".
- The atomic number increases from left to right in a period and from top to bottom in a column.
- Elements in the same period have the same principal quantum number n.
- Elements belonging to the same column (group) generally have the same external electronic structure, so they often have similar chemical or physical properties (don't generalize! there are some exceptions).

The periodic table is divided into 4 blocks according to the external electronic structure of the elements:
Bloc s : ns^1 or ns^2 ; columns 1 and 2.
Bloc p : ns^2, np^x (with : $1 \leq x \leq 6$) ; columns 13 to18.
Exception :
$_2He$ ($1s^2$) is classified in column 18 because of its properties, which are similar to those of the elements in this column (inert gases).
Bloc d: $(n\text{-}1)d^x$, ns^y (with : $1 \leq x \leq 10$ and $0 \leq y \leq 2$) ; columns 3 to 12 : "métaux de transition".
Bloc f: $(n\text{-}2)f^x$, $(n\text{-}1)d^y$, ns^2 with $n = 6$ ou 7, $0 \leq x \leq 14$; $y = 0$ or 1 or 1 or exceptionally 2 for $_{90}Th$).
Elements for which n = 6 are called "Lanthanides"; those for which n = 7 are called "Actinides" (the latter are all radioactive).

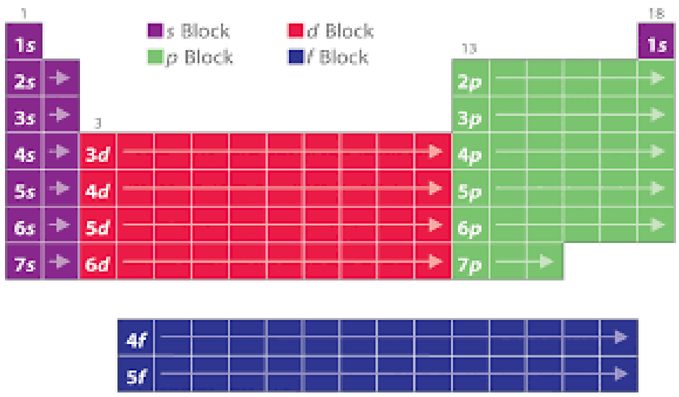


Table 1: Sub/Group A (electronic configuration of the outer layer)

columns	1	2	13	14	15	16	17	18
Group	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	$VIII_A$
outer layer	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Nbr of e^- valences	1	2	3	4	5	6	7	8

Table 2 : Sub/Group B (electronic configuration of the outer layer)

columns	3	4	5	6	7	8	9	10	11	12
Group	III_B	IV_B	V_B	VI_B	VII_B	$VIII_B$			I_B	II_B
outer layer	$ns^2(n\text{-}1)d^1$	$ns^2(n\text{-}1)d^2$	$ns^2(n\text{-}1)d^3$	$ns^1(n\text{-}1)d^5$	$ns^2(n\text{-}1)d^5$	ns^2 $(n\text{-}1)d^6$	ns^2 $(n\text{-}1)d^7$	ns^2 $(n\text{-}1)d^8$	$ns^1(n\text{-}1)d^{10}$	$ns^2(n\text{-}1)d^{10}$
Nbr of e^- valences	3	4	5	6	7	8	9	10	1	2

I-1 Families or groups (columns)

Column 1: alkalis

The external electronic structure is: ns^1 ⇒ they give monovalent cations : Na^+, K^+ ...

⇒ they give basic oxides: $Na_2O + H_2O \rightarrow 2\ NaOH$

Column 2: alkaline earths

The external electronic structure is: ns^2 ⇒ they give bivalent cations: Mg^{2+} , Ca^{2+} ...

⇒ they give basic oxides: $CaO + H_2O \rightarrow Ca(OH)_2$

Columns 3 to 12: transition metals

Their external electronic structure is: $(n-1)d^x$, ns^2 (ns^1 or ns^0) with $1 \leq x \leq 10$.

⇒ they give cations with multiple valences: Fe^{2+}, Fe^{3+}, Cu^+, Cu^{2+} ...

Columns 13 to 16: the family of non-metals

The external electronic structure of these elements is: ns^2, np^1 to ns^2, np^4

The elements in column 16 ⇒ give bivalent anions : O^{2-}, S^{2-}.

Column 17: halogens

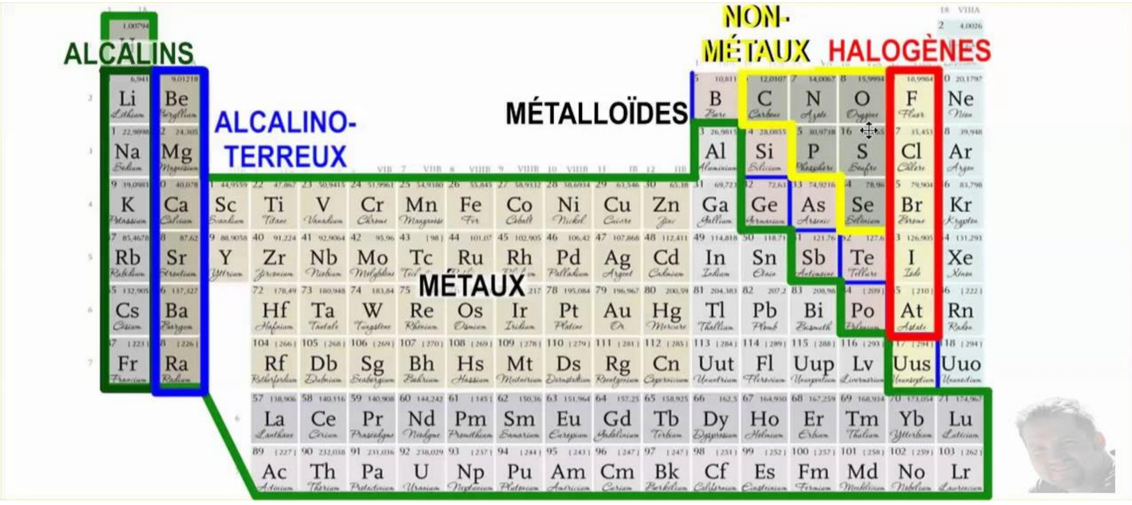
Their external electronic structure is: ns^2, np^5 ⇒ they give monovalent anions: F^-, Cl^-, Br^- ...

Column 18: rare gases

The external electronic structure is: ns^2, np^6, except for He ($1s^2$).

The rare gas configuration corresponds to saturation of the outer electronic layer:

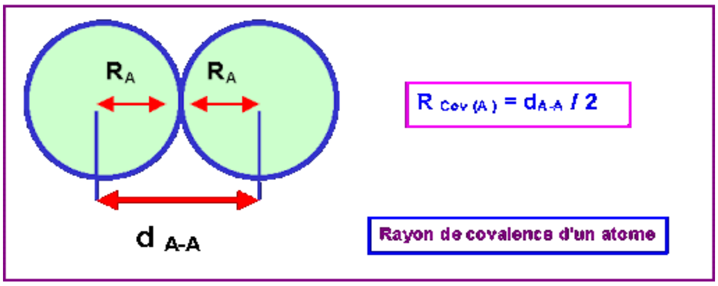
⇒ they have a high chemical inertia, but their reactivity increases with Z, for example Xenon ($_{54}Xe$) gives stable compounds when combined with highly electronegative atoms such as F and O (XeF_2, XeF_4, $XeOF_4$, XeO_3).



II- Atomic characteristics and periodicity.

II -1 Atomic radius (covalent radius) rc

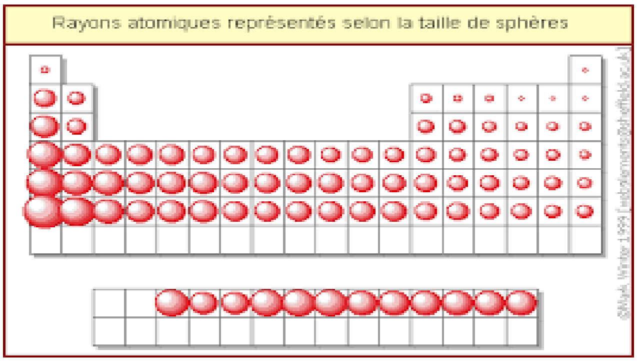
The atomic radius of an atom is equal to half the distance separating the 2 nuclei of a homonuclear diatomic molecule linked by a simple covalent bond.



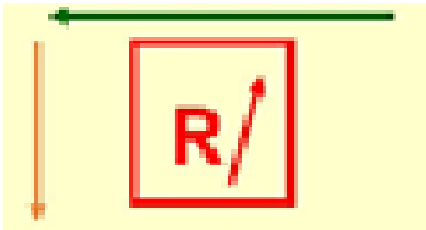
Note:

To determine the atomic radius of O we take half the distance O-O in H_2O_2 (g)

($dO-O$ = 148 pm) and not in $O_2(g)$ ($dO=O$ = 121 pm).



We can see that :
a) r_c decreases in one period (from left to right) and increases (from right to left)
b) r_c increases in a column (from top to bottom).



Meaning of increase of r in the periodic table.

II- 2- a-Variation de l'énergie d'ionisation E_i dans le tableau périodique

- Dans une colonne, lorsque Z augmente (en allant de haut en bas) :

- le nombre de couches augmente,
- la distance noyau - électron périphérique augmente (le rayon atomique augmente) ⇒ « **effet distance** »,
- la force d'attraction noyau - électron périphérique diminue (e– de plus en plus libre), l'énergie d'ionisation diminue.

II- 2 Ionization energy.

- E_{i1}, is the minimum energy that must be supplied to an isolated atom, A(g) (gaseous state), to strip it of an electron according to the reaction: : $A_{(g)} \xrightarrow{E_{i1}} A_{(g)}^{+} + e^{-}$ **$E_{i1} > 0$**
- E_{in} The nth ionization energy corresponds to the reaction:

$$A_{(g)}^{n-1} \xrightarrow{E_{in}} A_{(g)}^{n+} + e^{-} \quad \mathbf{E_{in} > E_{i1}}$$

II- 2- a-Variation of the ionization energy E_i in the periodic table

- In a column, as Z increases (from top to bottom) :

- The number of layers increases,
- The distance between the nucleus and the peripheral electron increases (the atomic radius increases) ⇒ "distance effect",
- The force of attraction nucleus - peripheral electron decreases (e- increasingly free), the ionization energy decreases.

Example:

$_3Li$: $1s^2$ / <u>$2s^1$</u>

$_{37}Rb$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$ / $\underline{5s^1}$

Distance effect: $E_{i1}(Rb) < E_{i1}(Li)$ d'ou E_{i1} (Rb) = 402 kJ.mol^{-1} ; E_{i1} (Li) = 520 kJ.mol^{-1}

- In one period, as Z increases (going from left to right) :

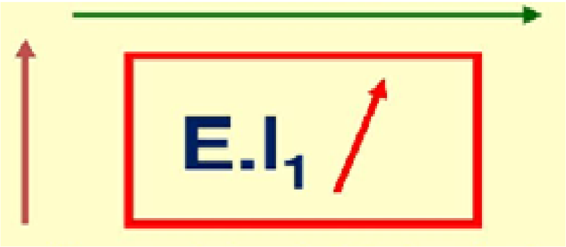
- The number of layers is the same; but Z increases (the number of + charges in the nucleus increases) ⇒ "**charge effect**",
- The force of attraction between the nucleus and the peripheral electron increases,
- The distance nucleus - peripheral electron decreases (the atomic radius decreases) the ionization energy increases.

Example:

$_3Li$: $1s^2$ / $\underline{2s^1}$ $_9F$: $1s^2$ / $\underline{2s^2\ 2p^5}$

Charge effect: $E_{i1}(F) > E_{i1}(Li)$ $E_{i1}(F)$ = 1681 kJ.mol^{-1} ; $E_{i1}(Li)$ = 520 kJ.mol^{-1}

E_{i1} varies in the opposite direction to the atomic radius



Meaning of increase of Ei in the periodic table.

II-3 Electronic affinity A or E_A:

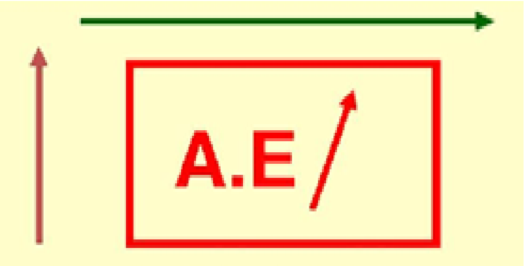
This is the opposite of ionization.
Electron affinity A, is the energy released (liberated) when an atom captures an electron.

$$X_{(g)} + e^- \rightarrow X_{(g)}^- + \boldsymbol{A} \text{ or } \boldsymbol{E_A} \text{ (It can be positive or negative).}$$

II- 3- a-Variation of the electronic affinity A in the periodic table:

- In a column, going from top to bottom, Z increases, the force of attraction nucleus - peripheral electron decreases, the atomic radius increases ⇒ **the electronic affinity** decreases (**distance effect**).
- In a period, (going from left to right) when Z increases, the force of attraction nucleus - peripheral electron increases, the atomic radius decreases⇒ **the electron affinity** increases (**charge effect**).

Electronic affinity varies with ionization energy and in the opposite direction to atomic radius in the periodic table.



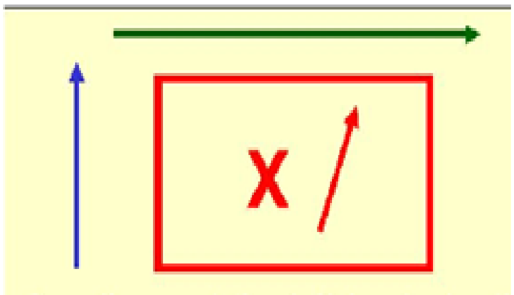
Meaning of increase of A or E_A in the periodic table.

II- 3 Electronegativity χ

This is a quantity that measures the tendency of an element to attract electrons towards it within a covalent bond ⇒ appearance of partial charges.

$$\mathbf{A\text{-}B} \rightarrow \mathbf{A}^{\delta+} + \mathbf{B}^{\delta-} \quad \text{(B is more electronegative than A).}$$

Electronegativity varies with ionization energy and in the opposite direction to atomic radius in the periodic table.



Meaning of increase of χ in the periodic table.

III- 3-a Electronegativity scales.

- **Millikan scale**.

This is defined on the basis of the ionization energy E_I and the electron affinity, E_A, by the relationship:

$$\chi = \frac{(E_I + E_A)}{2} \quad \text{(at } \mathbf{eV}\text{)}$$

- **Pauling scale.**

It is based on the dissociation energies of the bonds of simple diatomic molecules:
$E_{A\text{-}A}$, $E_{B\text{-}B}$ and $E_{A\text{-}B}$.
The difference in electronegativity between elements B and A is given by:

$$|\chi_A - \chi_B| = 0{,}102\sqrt{E_{A-B} - \sqrt{E_{A-A} . E_{B-B}}} \quad \text{at } \mathbf{Ev.}$$

With $E_{A\text{-}A}$, $E_{B\text{-}B}$ and $E_{A\text{-}B}$ are the dissociation energies of the molecules (A-B), (A-A) and (B-B).
0.102 coefficient that allows energies values in Kg/mol to be used and converted to eV/mol

- **Allred and Rochow**

Given by: $\chi = \frac{e^2 Z_{eff}}{r_{cov}^2}$ with Z_{eff}: effective charge of the nucleus;
e: elementary charge ;
r_{cov}: covalent radius of the element.

Note

Noble gases do not have electronegativity because their valence layer is saturated.

III Physical properties of the elements.

The periodic table is divided into three categories according to the metallic nature of the elements:

Metals

- These are located to the left and centre of the periodic table: blocks s (except H), d, f and one half of block p, **e.g.** Al, Sn, Pb, Bi, Po ....
- They are all solid at room temperature (25°C), except for mercury ($_{80}$Hg) which is liquid.
- They are good conductors of heat and electricity.

Non-metals

- They are located on the right of the periodic table: second half of the p block, e.g. F, O, N, C, P ....
- They are solid or gaseous at 25°C, exceptionally liquid (di-bromine, Br_2).
- They are poor conductors of heat and are electrical insulators. Except for carbon, which is insulating (diamond) or conductive (graphite).

Semi-metals

On the borderline between the two previous categories, they behave like semiconductors (Compounds whose conductivity increases with temperature, for example Silicon ($_{14}Si$) and Germanium ($_{32}Ge$) used in electronics).

Note:

Hydrogen does not belong to any chemical family. It is a molecular gas (H_2) at 25°C. It can give a positive ion (H^+), but also the hydride ion (H^-); so it behaves like a:

Metal ($H \rightleftarrows 1e^- + H^+$)
Non-metal ($H + 1e^- \rightleftarrows H^-$).

IV- Chemical recognition criteria
Metals give cations, their oxides are basic.
Example: $Mg \longrightarrow Mg^{2+}$ and $MgO + H_2O \longrightarrow Mg(OH)_2$
Non-metals give anions, their oxides are acidic.
Example: $S \longrightarrow S^{2-}$ and $SO_2 + H_2O \longrightarrow H_2SO_3$

V- Sanderson's rule:

An element is metallic if the number of electrons in its highest n layer is less than or equal to its period number. (Except H and Ge).

Examples

Mg: Z=12 so EC: [Ne] $3s^2 \longrightarrow$ 2 electrons on n=3 and belongs to period 3 so **Mg** is a metal.
Se: Z=34 therefore EC:[Ar] $4s^2 3d^{10} 4p^4 \longrightarrow$ 6 electrons on n=4 and belongs to period 4 therefore **Se** is a nonmetal.