Atomes et molécules

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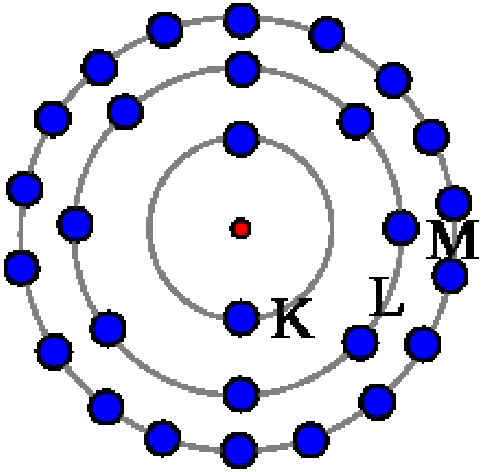
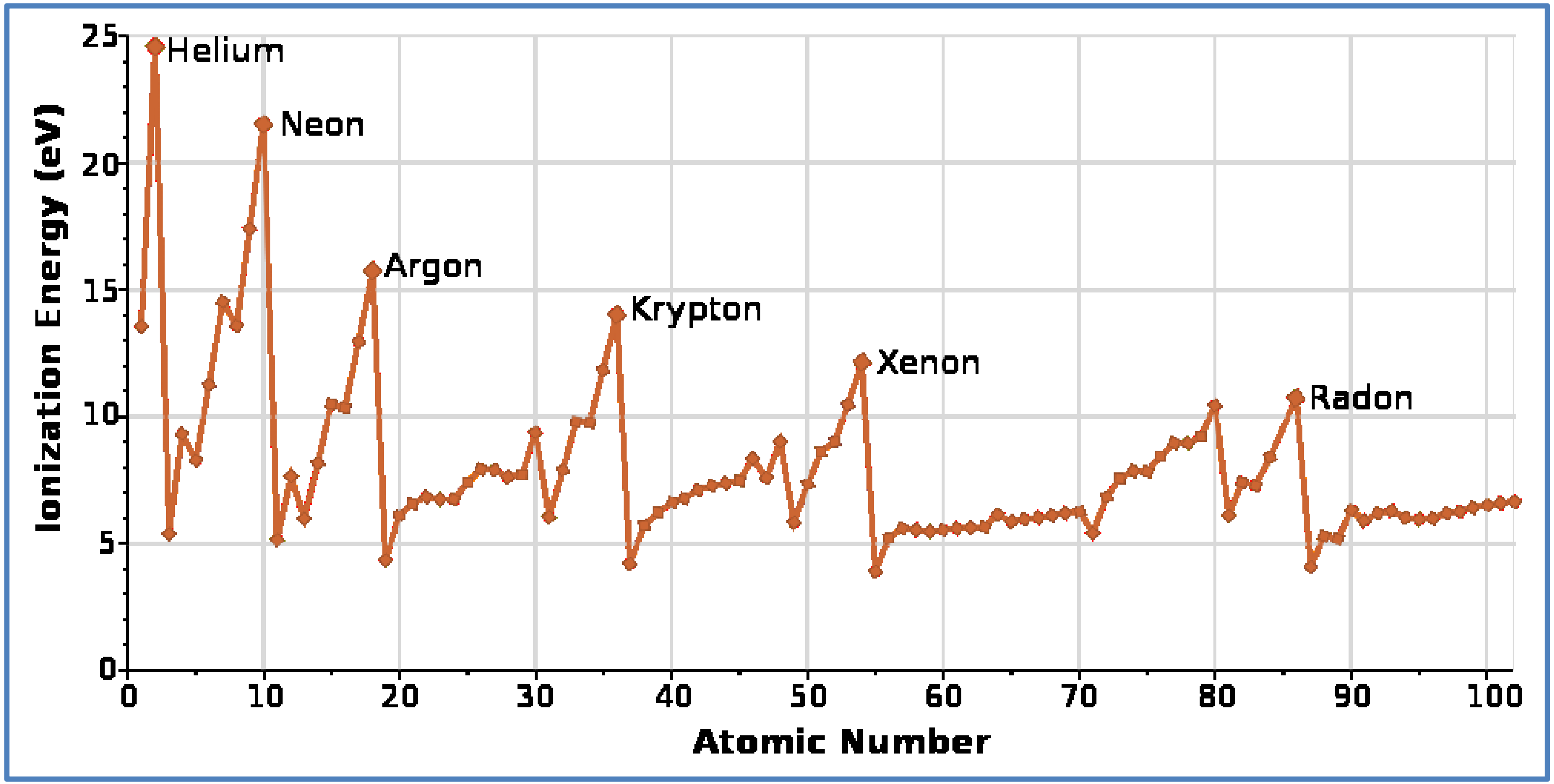
Chapter 5 : Periodic properties of atoms

1 – Atomic radius

2 – Formation of ions

2.1 Ionization energy
2.2 Electronic affinity
2.3 Electronegativity and Electro positivity
2.4 Most probable ions

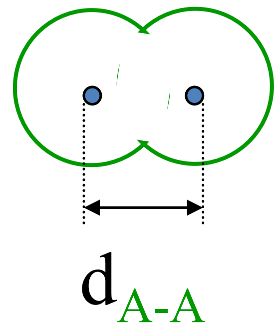




1) Atomic radius

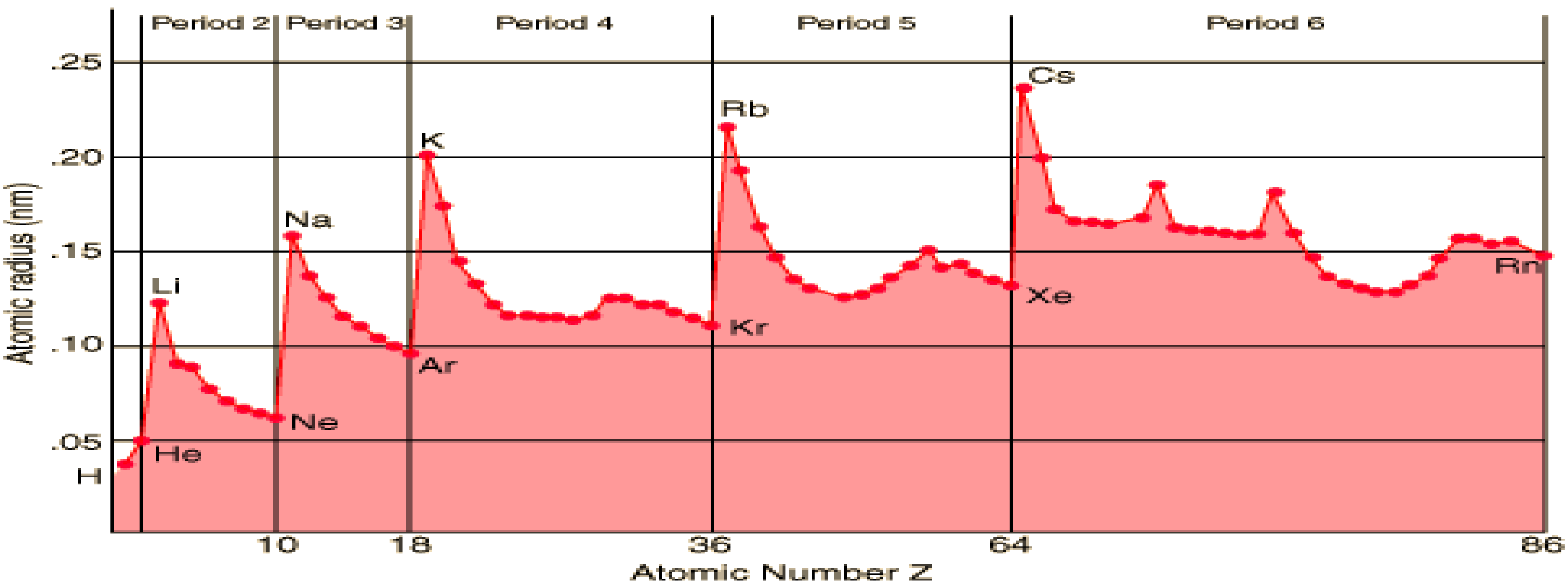
Covalent radius:

The covalent radius r_C of an atom **A** correspond to the half bond lengths in the molecules of the chemical compound **(A-A)**



$$r_C = d_{A-A}/2$$

$r_c(H) = d_{H-H}/2 = 0.074/2 = 0.037$ nm



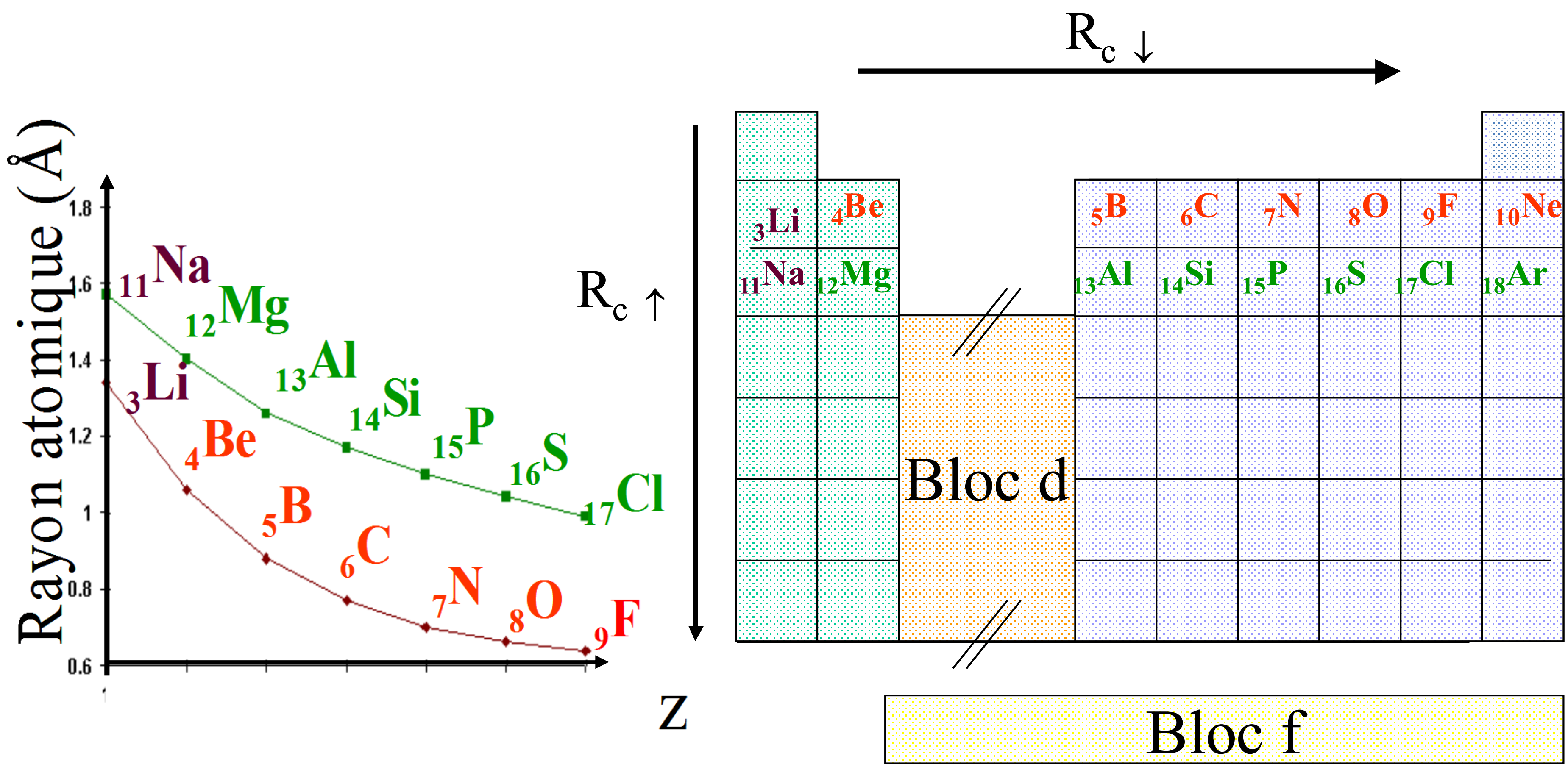
Variation of the covalent radius in the periodic table+

- In a given family (column), r_c increases when z increases

  n ↑ (shell number ↑)

- For a given period (row), r_c diminishes when z increases.

  same n but e-↑ ⇔ protons↑ ⇒ electrostatic attraction ↑



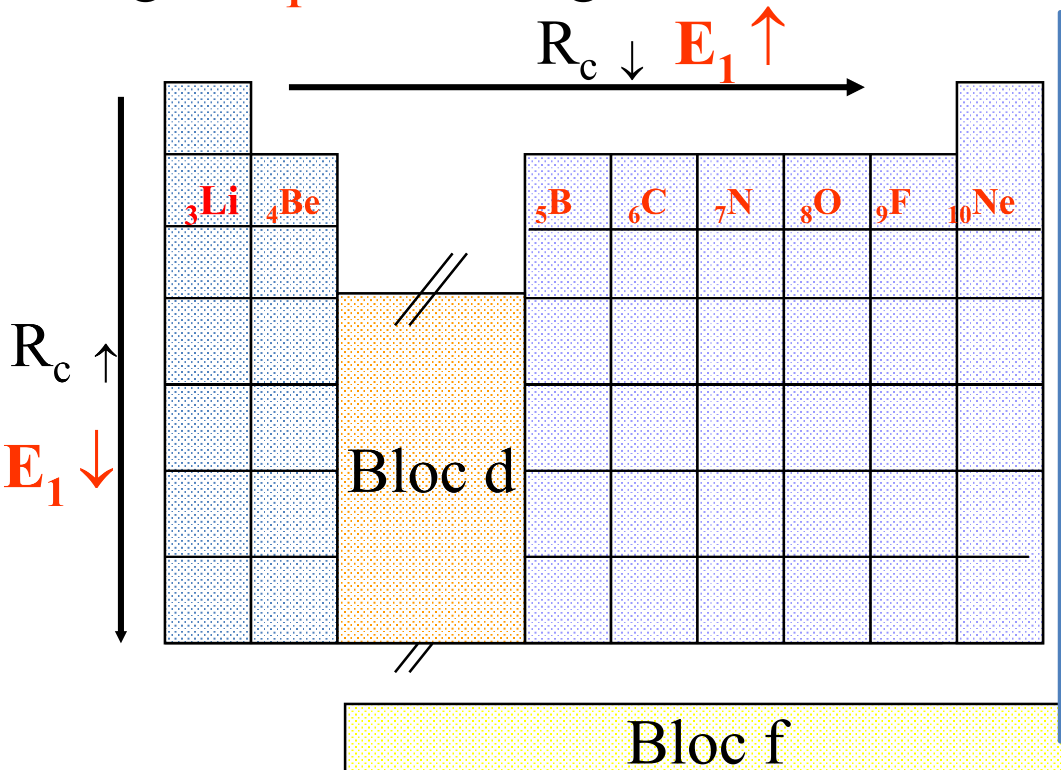
Chapter 5 – 2. Formation of ions

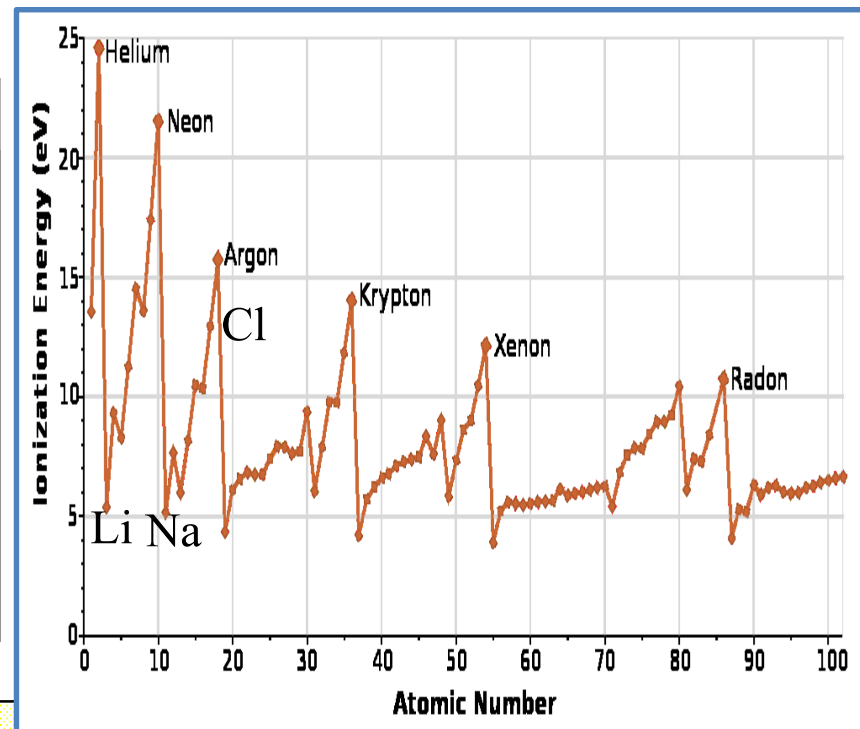
2-1) **Ionisation energy**

E_1 is the necessary energy to remove an electron from the atom X.

$$X \rightarrow X^+ + e^-$$

Extraction of a second (or more) electron is also possible but the energy is more and more important.
E_1 is larger when the attraction between the nucleus and the electron is stronger. **E_1** is thus larger when the radius is smaller.





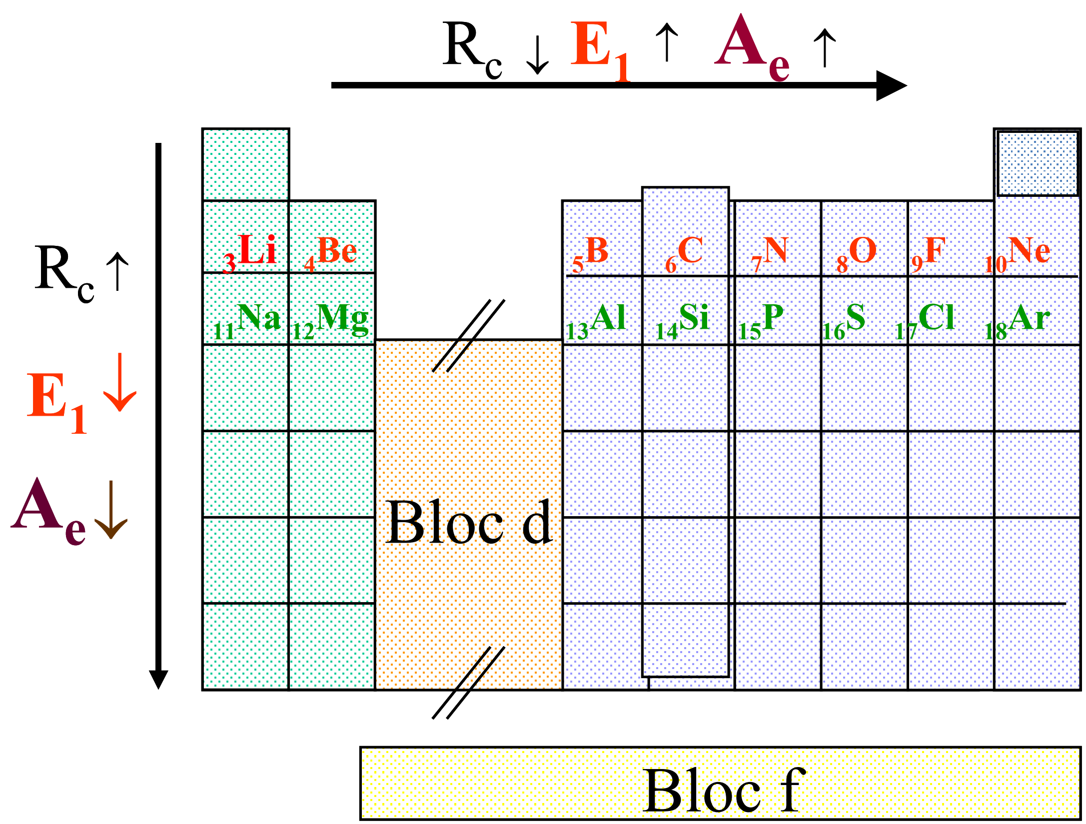
2-2) Electronic affinity (Ae)

$$\boxed{X + e^- \rightarrow X^-}$$

- The electron affinity is a measure of the energy change when an electron is added to a neutral atom to form a negative ion. For example, when a neutral chlorine atom in the gaseous form picks up an electron to form a Cl^- ion, it releases an energy of 349 kJ/mol. It is said to have an electron affinity of -349 kJ/mol and this large number indicates that it forms a stable negative ion. Small numbers indicate that a less stable negative ion is formed.
- Groups VIA (O, S) and VIIA (F, Cl) in the periodic table have the largest electron affinities.
- Alkali earth elements (Group IIA) and noble gases (Group VIIIA) do not form stable negative ions.

In general, **the electron affinity A_e** varies in the same direction as the ionisation energy E_1. Atoms which have strongly bounded electrons (large ionization energy) are able to capture one or more extra electrons.

But there are some exceptions

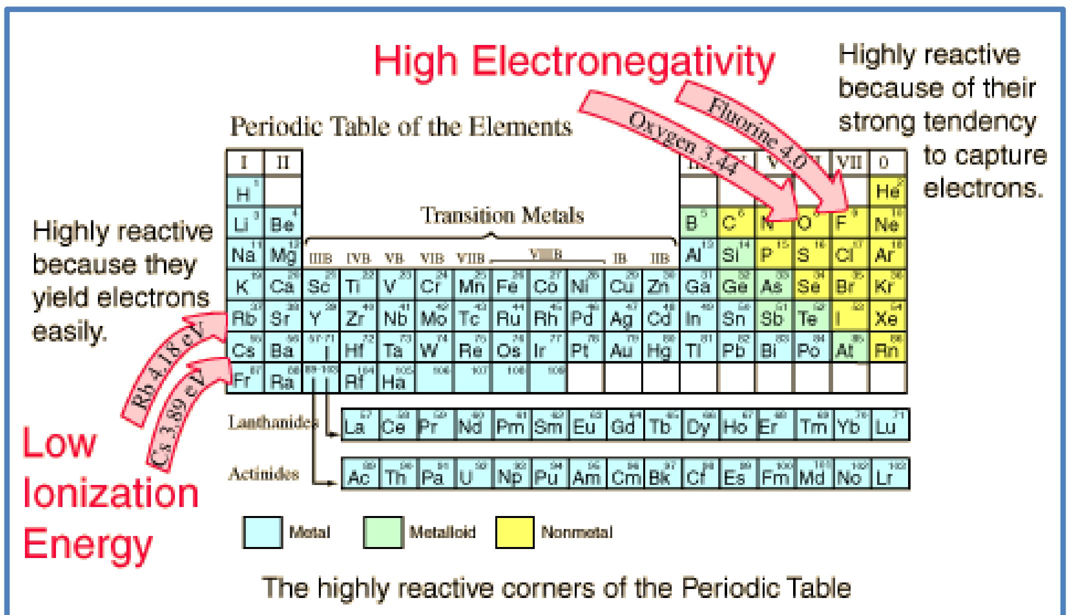


2.3. Electronegativity - Electropositivity

Chemical reactivity depends on electron attractive properties of atoms.

- Electronegativity E_- corresponds to the tendency of an atom to **attract** an electron. It is high among non–metals
- Electropositivity E_+ corresponds to the tendency of an atom to **loose** an electron (low ionization energy). Conductive metals

While E_1 and A_e correspond to isolated atom properties, $E-$ is important for the capacity of an atom to react chemically with other atoms.



Chapter 5 – 2. Formation of ions

Definitions of electronegativity:

- **Mulliken** : based on E_1 et A_e : $E^- = ½\,(E_1 + A_e)$
- **Pauling** : E^- (F) = 4 for Fluor, most electronegative element.

For other elements, the scale is relative to Fluor. The value of the least electronegative element is E^- (Cs) = 0,7 for Cesium.

Pauling Electronegativity Values

H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.3											Al 1.5	Si 1.9	P 2.2	S 2.6	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.8	Ge 2.0	As 2.2	Se 2.6	Br 2.8	Kr
Rb 0.8	Sr 0.9	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 1.9	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.5	Xe

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Chapter 5 – 2. Formation of ions

Consequences:

Most electronegative elements (tendency to become a negative ions) are good oxidizers. $X + e^- \rightarrow X^-$ **reduction reaction** = gain of an electron

Most electropositive elements (tendency to become a positive ions) are good reducers. $X \rightarrow X^+ + e^-$ **oxidation reaction** = electron loss

$$\text{Oxidant} + e^- \xrightarrow{\text{Reduction}} \text{Product}$$

(Electrons **gained**; oxidation number **decreases**)

$$\text{Reductant} \xrightarrow{\text{Oxidation}} \text{Product} + e^-$$

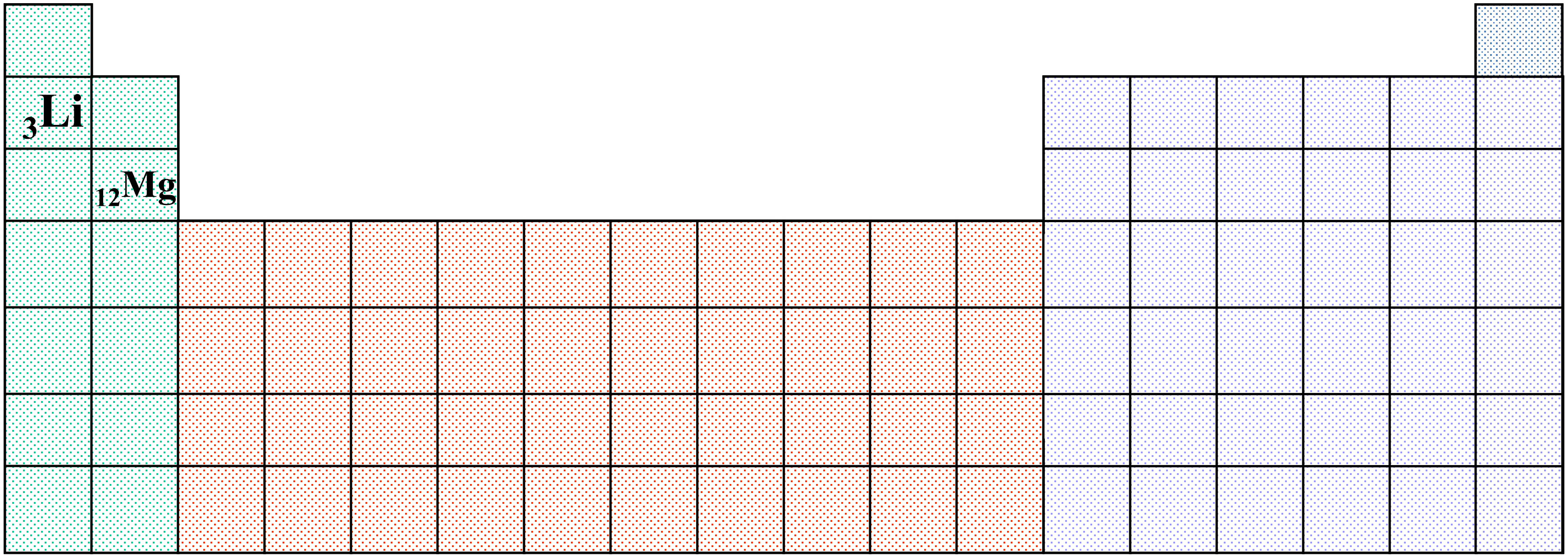
(Electrons **lost**; oxidation number **increases**)

That is, the oxidant (oxidizing agent) removes electrons from another substance, and is thus itself reduced. And, because it "accepts" electrons, the oxidizing agent is also called an electron acceptor. Oxygen is the quintessential oxidizer.

Electropositive elemental metals, such as lithium, sodium, magnesium, iron, zinc, and aluminium, are good reducing agents.

2-4) Most probables ions

Bloc s elements (ns^1 ou ns^2): tendency to loose an electron



$_{3}Li$ $1s^2\ 2s^1$

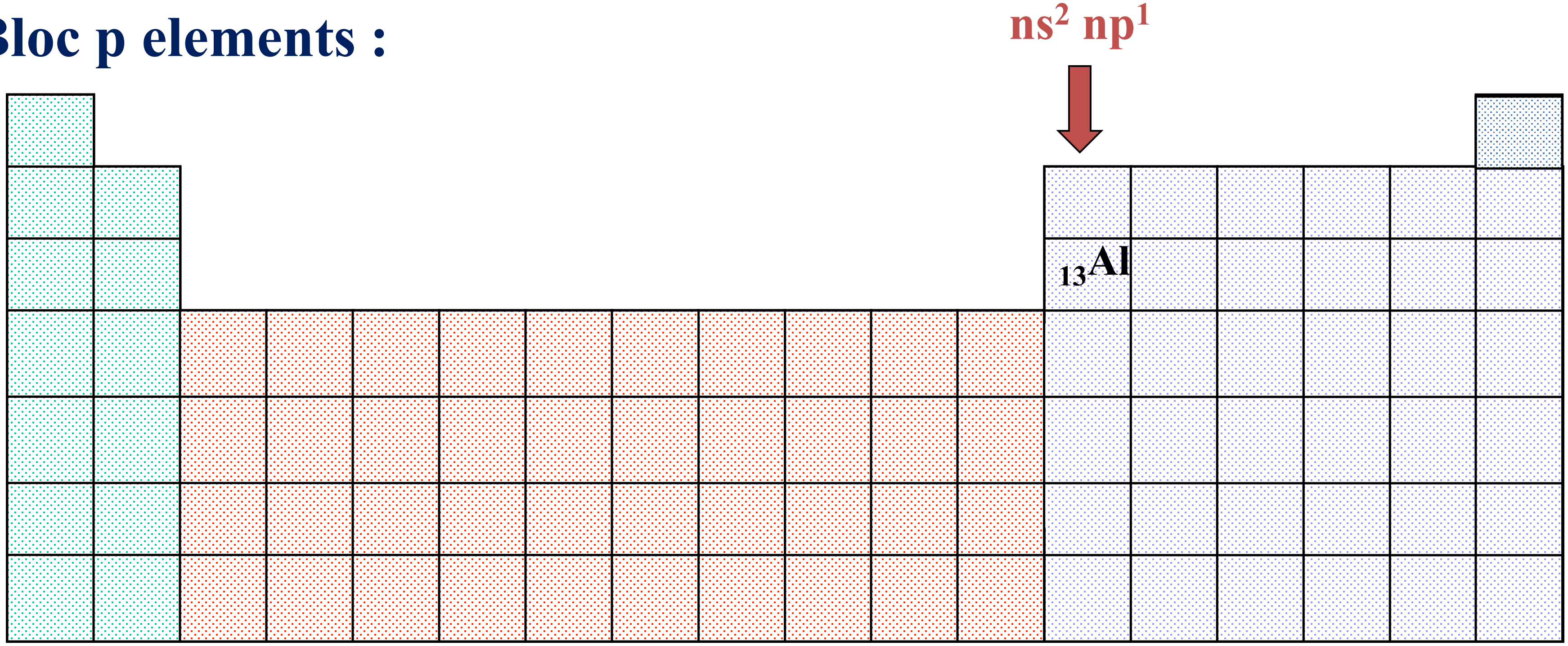
Li^+ $1s^2\ 2s^0$

$_{12}Mg$ $1s^2\ 2s^2\ 2p^6\ 3s^2$

Mg^+ $1s^2\ 2s^2\ 2p^6\ 3s^1$

Mg^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^0$

Bloc p elements :



(ns^2 np^1): tendency to loose s and p electrons in order to empty the shell n =3.

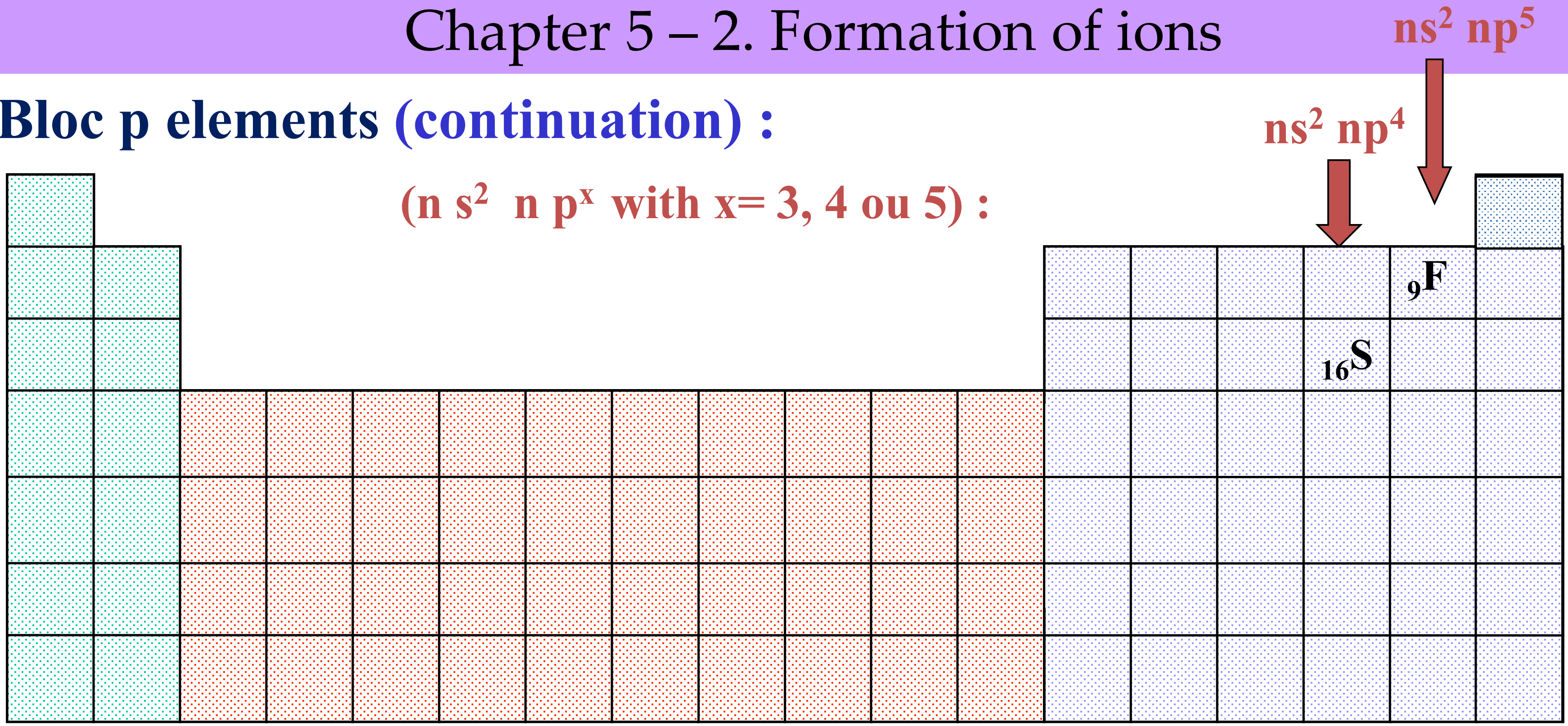
Exemple: Aluminium Al (Z=13)

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

Al^{3+} $1s^2\ 2s^2\ 2p^6$

Bloc p elements (continuation) :

(n s^2 n p^x with x= 3, 4 ou 5) :



Tendency to gain electrons in a way to saturate the p shell (= filled with 8 electrons).

Exemples : Fluorine (Z=9) becomes an ion F^-

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

F^- $1s^2\ 2s^2\ 2p^6$

Sulfur (Z=16) becomes an ion S^{2-}

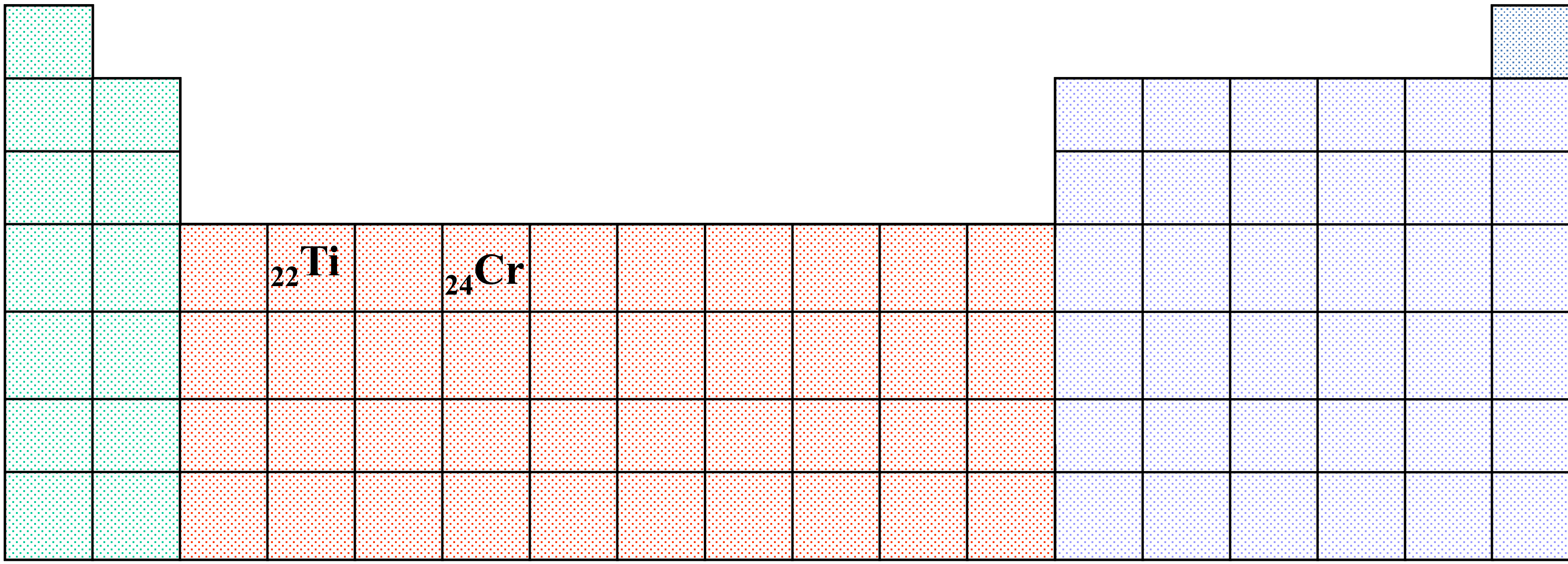
$_{16}S$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

S^{2-} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Chapter 5 – 2. Formation of ions

Bloc d elements (transition elements) :

Tendency to loose electrons first from s subshell with highest n value before eventually loosing electrons from (n-1)d subshell.



$_{22}Ti$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$

Loosing 1 electron ⟷ Ti^+ … $4s^1\ 3d^2$

Loosing 2 electrons ⟷ Ti^{2+} … $4s^0 3d^2$

Loosing 3 electrons ⟷ Ti^{3+} … $4s^0\ 3d^1$

3 stable cations

Chromium !!!!!: **Cr^{3+} is an oligoelement** essentiel for our metabolism.
Cr^{6+} is toxic

Conclusions:

- **For s and p block elements :**

Cations and anions adopt the electronic configuration of the closest rare gas.

- **For d block elements :**

Cations are formed and can take variable charges.

QCM 06 : De quelle(s) sous-couche(s) est (sont) arrachés les électrons lorsqu'un atome de fer devient chargé « +3 » sous forme de Fe^{3+} ? Fe ($Z = 26$)

- **a.** 3d seulement
- **b.** 3p seulement
- **c.** 4s et 3d
- **d.** 3s et 4d
- **e.** 4s et 3p

QCM 07 On considère les atomes suivants : Al ($Z = 13$), Si ($Z = 14$), P ($Z = 15$) et S ($Z = 16$). Quelle(s) proposition(s) est(sont) exacte(s) :

- **a.** Aucun de ces 4 atomes n'est un métal
- **b.** L'électronégativité de l'atome d'aluminium, Al, est plus grande que celle de l'atome de soufre, S
- **c.** L'énergie de première ionisation de l'atome de silicium, Si, est plus grande que celle de l'atome de phosphore, P
- **d.** L'affinité électronique de l'atome de silicium, Si est plus grande que celle de l'atome de phosphore, P
- **e.** Aucune des propositions précédentes (A à D) n'est exacte