

6th Course of Chemistry 1

The principles governing the electronic structure of an atom:

- To describe an atom, we have the atomic number Z , which characterizes the charge of the nucleus and determines the number of electrons occupying the different energy levels of the atom.
- The arrangement of electrons on the different levels depends on 3 factors.

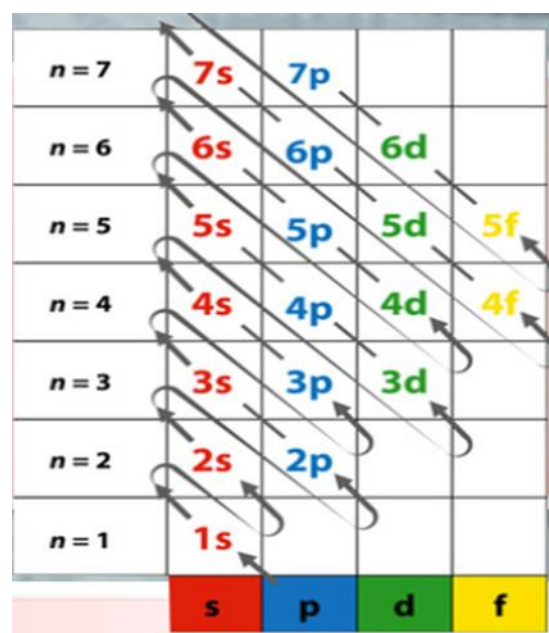
1) Principle of stability (Klechkowski's rule)

2) Pauli's exclusion principle

3) Hund's rule

1) Principle of stability (Klechkowski's rule)

- Electrons occupy, in the ground state, the lowest energy level, which gives the atom minimal energy and maximum stability.
- The filling order of sublevels obeys Klechkowski's rule.
- The filling order of the various layers and sublayers is done by increasing value of $n+1$.
- For the same value of $n+1$, they will be classified in order of increasing n .



Parallel lines are drawn and the beginning of the arrow is read to the end.

The energy order of the atomic orbitals (AO) of a poly-electronic atom is as follows:



2) Pauli's exclusion principle

"Two electrons of the same atom cannot have their four quantum numbers identical.

Examples:

${}_2\text{He}$: contains 2 electrons.

e_1 : $n=1 \Rightarrow l=0, \Rightarrow m=0 \Rightarrow s = +1/2 \Rightarrow (1,0,0,+1/2)$ 1s



e_2 : $n=1 \Rightarrow l=0, \Rightarrow m=0 \Rightarrow s = -1/2 \Rightarrow (1,0,0,-1/2)$



- It is impossible to have the same 4 numbers.
- The electrons will necessarily have antiparallel spins (opposite directions).
- Based on Klechkowski's rule, the electrons are positioned in such a way that the total energy is as small as possible: this is the so-called fundamental state.

Examples :

3d : ($n=3$ and $l=2$) $n+l=5$

4s : ($n=4$ and $l=0$) $n+l=4$

Since $n+l(4s) < n+l(3d)$ so **4s is filled before 3d**

Overlapping phenomenon. (Phénomène de chevauchement.)

4f : ($n=4$ and $l=3$) $n+l=7$

5d : ($n=5$ and $l=2$) $n+l=7$

Since **the two orbital has the Same value of $n+l$** ; *The lowest energy level is the one with the lowest value of n .* so We fill 4f before 5d

Orbital	l	m	Quantum box Case quantique	Max. number of electrons	
s	0	0		2	S²
p	1	-1,0,1		6	P⁶
d	2	-2,-1,0,1,2		10	d¹⁰
f	3	-3,-2,-1,0,1,2,3		14	f¹⁴

3- Hund's Rule

In a given energy sublevel, the number of unpaired (single) electrons must be maximized. Electrons that can be distributed across an atom's orbitals tend to occupy the maximum number of orbitals defined by the same number of electrons, before completely saturating each orbital. Electrons are placed to obtain the greatest possible multiplicity (maximum of parallel spins).

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p \dots$

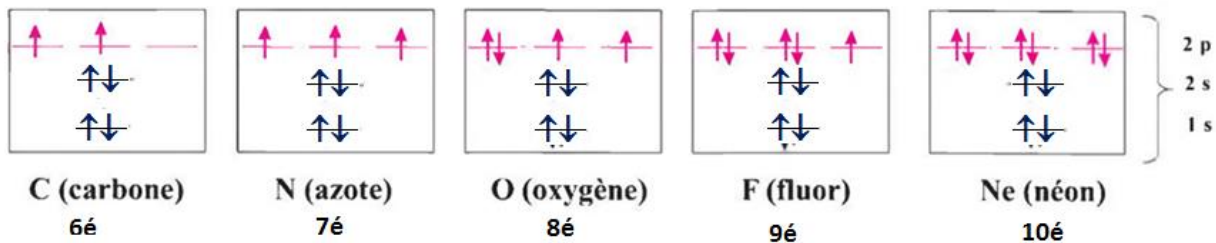
Examples:



Exact form



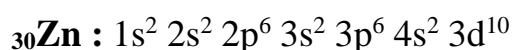
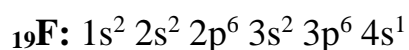
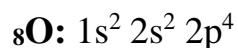
- Hund's rule is applied: the electrons are placed in such a way as to obtain the greatest possible multiplicity (maximum number of parallel spins). This set of precepts is illustrated in the figure below for elements ranging from carbon to neon.



Exercise

1) Give the electronic configuration of the following elements: ${}_{8}\text{O}$, ${}_{19}\text{F}$; ${}_{30}\text{Zn}$

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p \dots$



2) The following sets of quantum numbers are assumed to each determine an orbital. However, one of the sets is wrong. Which is it? And tell us why.

(a) $(n, l, m, s) = (3, 0, 0, +1/2)$ **true 3s**

(b) $(n, l, m, s) = (2, 1, -1, +1/2)$ **true 2p**

(c) $(n, l, m, s) = (1, 0, 0, +1/2)$ **true 1s**

(d) $(n, l, m, s) = (4, 1, -2, +1/2)$ **false**

$$\begin{aligned} \blacktriangleright n = 4 \Rightarrow l = 0, 1, 2, 3 \Rightarrow l = 0 \Rightarrow m = 0 \\ \Rightarrow l = 1 \Rightarrow m = -1, 0, +1 \end{aligned}$$

Choice (d) is wrong because, for $l=1$, the possible values of m are only $m = -1, 0, +1 \Rightarrow m \neq -2$

Exceptions to Klechkowski's rule

➤ For a multiplicity of electrons, the most stable state manifests itself in orbitals of equal energy, which must be half or completely filled. Atomic orbitals have a maximum or minimum spin. This case appears in distributions :



Examples

- Chromium (period 4) ${}_{24}\text{Cr}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

- Copper (period 4) ${}_{29}\text{Cu}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

- Silver (period 5) ${}_{47}\text{Ag}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^{10}$

These examples show that the possibility of saturating an orbital sometimes takes precedence over the rule, especially for orbitals from $n = 3$ or 4.

Finally, the noble gases (Neon, Argon, Krypton, etc.) are never exceptions to Klechkowski's rule. They can therefore be taken as references from the point of view of electronic configuration.

The configuration of copper, for example, can be written as follows:

${}_{29}\text{Cu}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ as well as : ${}_{18}[\text{Ar}] 4s^1 3d^{10}$

where "[Ar]" symbolises the electronic configuration of argon.

Valence and core electrons

Given the layered organization of the electron cloud, it is reasonable to distinguish between **the inner layers** - *with very negative energies* - strongly attached to the nucleus, and **the outer layer** describing peripheral electrons that are less bound due to the screening effect of the inner layers, and therefore more labile.

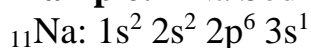
The energies involved in modifying the inner layers are also much higher than those that could affect the peripheral electrons.

In the writing of electronic configurations, this distinction is made by defining two categories of electrons:

Core electrons are those that populate the inner orbitals. For a given element, they correspond to the configuration of the noble gas preceding that element in the classification. The configuration of core electrons is symbolized by the noble gas symbol in parentheses.

Valence electrons populate the orbitals of the occupied peripheral layers. The valence configuration is traditionally noted by aligning the symbols of the subshells and by placing the number of electrons in the subshell as an exponent.

Example: ^{11}Na Sodium ($Z=11$)



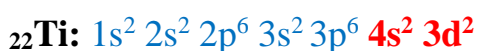
core electrons

valence electrons

The previous rare gas is neon ($Z = 10$)

The complete configuration is $[\text{Ne}] 3s^1$

Example: Titanium ($Z = 22$)



There are therefore **18 core electrons** and **4 valence electrons**.

The preceding rare gas is argon Ar ($Z = 18$).

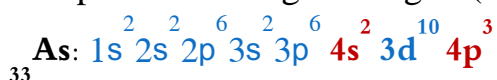
The configuration is written as $([\text{Ar}] 4s^2 3d^2)$.

The valence electrons here belong to different layers.

The **3s** and **3p** sublayers are **core layers** and the **4s** and **3d** **valence sublayers**.

Example: Arsenic ($Z=33$)

The previous rare gas is argon ($Z=18$). The configuration is written in the form



➤ **28 core electrons** and **5 valence electrons**.

➤ In this case, the full $3d^{10}$ sublayer is often considered to be an inert, internal sublayer.