Academic year 2023/2024 1st Year LMD



8th Course of Chemistry 1

8-1) Classification of the elements

The old classification shows the periodic table as being made up of 18 columns comprising

sub-groups A and B. Elements in the same group or family have the same number of electrons on the outer layer, which confers equivalent properties from a chemical point of view.

1) Subgroup A: elements in columns 1, 2, 13, 14, 15, 16, 17 and 18

block s and *block p* belong to subgroup A. Their electronic configurations always end with an s or p sub-layer.

| Group | I_A | Π_{A} | $\mathrm{III}_{\mathrm{A}}$ | IV _A | V _A | VI _A | VII _A | VIII _A | |
|----------------------------|-------|-----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--|
| Couche de Valence | ns | ns ² | ns ² np ¹ | ns ² np ² | ns ² np ³ | ns ² np ⁴ | ns ² np ⁵ | ns ² np ⁶ | |
| Nbre d' e de valence | 1 2 3 | | 3 | 4 5 | | 6 | 7 | 8 | |
| Colonne | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 | |
| Famille | | | | | | | | | |

The number in Roman numerals is the number of electrons that can participate in the bonds (number of valence electrons).

2) Sub-group B :

The elements in columns 3, 4, 5, 6, 7, 11 and 12 (d block) belong to sub-group B, their electronic configurations ending in a d sub-layer.

| colonne | Nbre d'e de valence | Couche de Valence | Groupe | COTOTING |
|---------|------------------------|----------------------|---------|----------|
| | e | | | |
| 1 | 1 | ns^{1} (n-1) | I_{B} | ر |
| | |)d ¹⁰ | | |
| 2 | 2 | ns² (n- | II | - |
| | | $-1)d^{10}$ | В | , |

| Colonne | Nbre d'e de valence | Couche de Valence | Groupe |
|---------|------------------------|---|---------------------------|
| 3 | 3 | $ns^2 (n-1)d^1$ | III _B |
| 4 | 4 | $ns^2 (n-1)d^2$ | IV_B |
| 5 | 5 | $ns^2 (n-1)d^3$ | \mathbf{V}_{B} |
| 6 | 6 | $ns^2 (n-1)d^4$ | VI_B |
| 7 | 7 | $ns^2 (n-1)d^5$ | VII _B |
| 8 | 8,9,10 | $\begin{array}{c} ns^2 \; (n{-}1)d^6 \\ ns^2 \; (n{-}1)d^7 \\ ns^2 \; (n{-}1)d^8 \end{array}$ | VIII _B |

8-2) Position of the element in the periodic table

8-2-1) Old classification

The positioning of the element is based on the configuration of the outer layer.

- **Period**: number of the outer layer = nmax

- Group: the number of valence electrons.

- Subgroup A: if the configuration ends in an ns or np orbital.

- Subgroup B: if the configuration ends in a d orbital.

For elements belonging to sub-group B (d block), the valence layer will be of the form ns^{x} (n-1)d^y.

 \blacktriangleright The sum (x + y) of the electrons will tell us the group of the element:

* When $3 \le x+y \le 7$, the corresponding elements belong to groups IIIB, IVB, VB, VIB and VIIB.

* When $8 \le x + y \le 10$, the corresponding elements belong to group VIIIB.

When **x** + **y** > 10:

if $ns^{1}(n-1)d^{10}$: the elements will belong to subgroup IB

if $ns^{2}(n-1)d^{10}$: the elements belong to subgroup IIB

Examples :

1) $_{3}\text{Li}:1s^{2}2s^{1}$

Period: number of the outer layer = nmax = 2**Group:** number of valence electrons = 1 valence electron the configuration ends with an *ns orbital* \Rightarrow subgroup A

2) $_{37}$ Rb : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 / 5s^1$: *Period:* number of the outer layer = nmax = 5 *Group:* number of valence electrons = 1 valence electron the configuration ends with an *ns orbital* \Rightarrow sub-group A. period = 2 Group (column) = I_{AA}

period = 5 Group (column) = I_{AA}

3) $_{7}N : 1s^{2}/2s^{2}2p^{3}$ *Period:* nmax = 2 $\frac{\text{period} = 2}{\text{Group (column)} = V_{AA}}$

Group: number of valence electrons = 5 valence electron the configuration ends with an *np orbital* \Rightarrow *subgroup A*.

4) 2) $_{23}$ V : 1s² 2s² 2p⁶ 3s² 3p⁶ / <u>4s² 3d³</u>

Period: max = 2

Group: 5 valence electron the configuration ends with an (n-1)d orbital \Rightarrow subgroup B period = 2 Group (column) = V_{BA}

 ${}_{26}Fe: 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} / 4s^{2} 3d^{6} \text{ period} = 4 \text{ group} = 8 \text{ él. valence} = VIII_{B}$ ${}_{27}Co: 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} / 4s^{2} 3d^{7} \text{ period} = 4 \text{ group} = 9 \text{ él. valence} = VIII_{B}$ ${}_{28}Ni: 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} / 4s^{2} 3d^{8} \text{ period} = 4 \text{ group} = 10 \text{ él. valence} = VIII_{B}$ The triad

8-2-2) Positioning according to the current classification.

> If the configuration ends with an *s* or *d* orbital:

The period = nmax = the last shell *The column* = Nv (valence electron count)

> If the configuration ends with a *p orbital*:

The period = nmaxThe column = Nv + 10

 If the configuration ends with a *p* orbital with saturated *d* orbital : *The period* = nmax *The column* = Nv

Examples: ${}_{15}P: 1s^{2} 2s^{2} 2p^{6} / 3s^{2} 3p^{3} \qquad p \text{ orbital} \Rightarrow Nv + 10$ period = 3 $column : Nv + 10 = 5 + 10 = 15 \Rightarrow \qquad period = 3$ column = 15 ${}_{6}C: 1s^{2} / 2s^{2} 2p^{2} \Rightarrow \qquad period = 2$ column = 10 + 4 = 14 period = 3 $column = N_{v} = 1$

| $Ti: 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} / 4s^{2}$ | period = 4 column = N _v = 4 | | | | | | | | |
|---|---|-----------------|----------------------|-----------|----|----|----|--|--|
| $Mn : 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} / 4s$ | period = 4 column = $N_v = 7$ | | | | | | | | |
| Ar: $1s^{2} 2s^{2} 2p^{6} / 3s^{2} 3p^{6}$ | | period colum | d = 3 $d = N_v +$ | - 10 = 18 | | | | | |
| Level n | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | |
| Layer | K | L | М | Ν | 0 | Р | Q | | |
| Maximum number of electron 2 n ² | 2 | 8 | 18 | 32 | 50 | 72 | 92 | | |

An electronic configuration is written as a function of the K, L and M layers.....

$${}_{6}^{C} : 1s^{2} / 2s^{2} 2p^{2} \implies {}_{6}^{C} : : K^{2} L^{4}$$

$${}_{15}^{P} : 1s^{2} / 2s^{2} 2p^{6} / 3s^{2} 3p^{3} \implies {}_{15}^{P} : K^{2} L^{8} M^{5}$$

$${}_{11}^{Na} : 1s^{2} 2s^{2} 2p^{6} / 3s^{1} \implies {}_{11}^{Na} : K^{2} L^{8} M^{1}$$

$${}_{22}^{Ti} : 1s^{2} / 2s^{2} 2p^{6} / 3s^{2} 3p^{6} / 4s^{2} 3d^{2} \implies {}_{22}^{Ti} : K^{2} L^{8} M^{10} N^{2}$$

$${}_{25}^{Mn} : 1s^{2} 2s^{2} 2p^{6} / 3s^{2} 3p^{6} / 4s^{2} 3d^{5} \implies {}_{25}^{Mn} : K^{2} L^{8} M^{13} N^{2}$$

$${}_{18}^{Ar} : 1s^{2} / 2s^{2} 2p^{6} / 3s^{2} 3p^{6} \implies {}_{18}^{Ar} : K^{2} L^{8} M^{10}$$

This type of configuration has only a limited interest: that of introducing the notion of electronic configuration with a view to creating Lewis structures. The most interesting method is that of atomic orbitals.

Electronic configuration of an ion

> Case of anions

Add one or more electrons to the electronic configuration of the atom in its ground state, following the rules of Klechkowski, Pauli and Hund.



2) Cations

Elimination of one or more electrons from the electronic configuration of the atom in its ground state, in accordance with the rules of Klechkowski, Pauli and Hund.



The 4s sublayer "empties" before the 3d sublayer.

 $\Rightarrow \mathrm{Fe}^{2^{+}}: [_{18}\mathrm{Ar}] 4\mathrm{s}^{0} 3\mathrm{d}^{6}$ ${}_{26}\mathrm{Fe}^{3^{+}}: [_{18}\mathrm{Ar}] 4\mathrm{s}^{0} 3\mathrm{d}^{5}$

Identical reasoning for compounds with electrons in their 4d, 4f or 5f sublayer. The 5s, 6s or 7s sublayer is emptied first.

Application exercises; I-

A-Determine the position in the periodic table from the electronic structure:

The electronic structure, in their ground state, of the following atoms is given:

- 1) He: K (2)
- 2) P: K (2) L (8) M (5)
- 3) C: K (2) L (4)
- 4) Ar: K (2) L (8) M (8)
- 5) Be: K (2) L (2)
- 6) Na: K (2) L (8) M (1)

B-Determine the period and column of the Classification to which each of the elements belongs.

> Correction

a. He : K(2) : first period and eighteenth column (or eighth column of the reduced classification)

classification) rare gas

b. P: K(2) L(8) M(5): third period and fifteenth column (or fifth in the reduced reduced classification)

c. C : K (2) L (4) : second period and fourteenth column (or fourth of the reduced classification)

d. Ar: K (2) L (8) M (8): third period and eighteenth column (or eighth column of the reduced classification)

reduced classification) rare gas

e. Be: K (2) L (2): second period and second column.

f. Na: K (2) L (8) M (1): third period and first column, alkali metal

II-

Placing an element in the Periodic Table :

Consider an element X with atomic number Z = 14.

1. Draw up the electronic structure of the corresponding atom in its ground state.

- 2. Deduce the period and column of the Classification to which X belongs.
- 3. Find the name and symbol of this element.

Correction

Given an element X with atomic number Z = 14.

1. Electronic structure of atom X: K (2) L (8) M (4)

2. Period and column of the Classification to which X belongs: it belongs to the third period and the fourteenth column (It is below carbon: it has the same number of electrons on the outer electronic layer).

the outer electronic layer)

3) Name and symbol of this element: Silicon, symbol Si.

Evolution of physical properties within the periodic table:

> Atomic radius - Ionization energy - Electron affinity

1- Definition

 $R_{a}(A) = R_{c}(A) = \frac{d_{(AA)}}{2}$

The periodicity of the properties of elements in the periodic table corresponds to the way in which the physical and chemical properties of elements repeat regularly from one period to another.

2- Atomic radius Ra or Covalent radius Rc

It corresponds to half of the distance between two identical atomic nuclei bonded by a covalent bond.

Its value can be obtained through experimental measurements or calculated from theoretical models.



When moving from left to right on the same row (period) of the periodic table,

electrons are added to the same shell. As the effective nuclear charge increases, the electrons experience a stronger attraction, causing the atoms to become more compact and thus the atomic radius decreases.

On the same period: if **Z** increases, then **Ra** decreases ;

If $\mathbb{Z} \nearrow \mathbb{F}_{att}$ attractive force $\nearrow \mathbb{R}_a \searrow$

When moving down a column from top to bottom, the number of valence electrons increases because the number of shells increases, and consequently the atomic radius increases.

On the same column: if Z increases, then Ra increases

 $Z \nearrow n \nearrow \Rightarrow$ volume, thus electron cloud increases and Ra \nearrow

 $\blacktriangleright \quad On \ the \ same \ period : Si \ \mathbf{Z} \nearrow \Rightarrow \mathbf{Ra} \ \mathbf{\Sigma}$

> On the same column : Si Z > le n > Ra >

3- Ionisation energy Ei or ionisation potential (IP)

To understand the finer details of the periodic table and chemical behaviour, we need a more precise idea of the energy with which an atom retains its electrons. This can be obtained using ionisation energy measurements.

Definition :

The first ionisation energy Ei of an element A is the minimum energy required to strip an electron from the neutral element A in the gaseous state:

 $A(g) \rightarrow A^+(g) + 1$ e- E₁: Energy of first ionisation

The second ionisation energy E2 is the minimum energy required to strip an electron from the charged cation once :

 $A+(g) \rightarrow A++(g) + 1$ e- E2: Energy of second ionisation

For a given period, the ionisation energy increases with the atomic number Z, from alkaline to noble gas,

The following table shows the Ei for some common elements. Values are given in eV.

| Atome | н | С | N | 0 | F | Ne | Li | Na | к | Mg | Ca |
|-------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|
| PI | 13,60 | 11,26 | 14,53 | 13,61 | 17,42 | 21,56 | 5,39 | 5,14 | 4,33 | 7,64 | 6,11 |

- Note that ionisation energy is a positive quantity: energy must be supplied to ionise an atom.
- Note that the energy of first ionisation increases overall from left to right in a row and increases from bottom to top in a column.
- > Over a period: Z increases : if $Z \land \Rightarrow F$ att $\land \Rightarrow E_1 \land$
- > On a column: if Z increases then Ra increases if Z > le n > E_1 >
 - $\succ Over a period: if Z \nearrow \Rightarrow E_1 \nearrow$
 - > On a column: if Z > le n > ⇒ E_1 >

Electronegative and electropositive elements

The table above shows two main families of elements:

Those which lose an electron with difficulty (O, F) and are therefore called electronegative.

Those that lose an electron very easily (such as the metals Li, Na, etc.) are called electropositive, in the sense that they easily produce a positive ion.

Electronic affinity EA

The first thing to define is the energy of electron attachment or energy of first attachment, known as Eatt. It represents the energy involved in providing (attaching) an extra electron to an atom in the gaseous state, as follows:

$$X(g) + e^- \longrightarrow X^-_{(g)}$$

This energy is often negative (Eatt < 0), so the reaction is often exothermic.

In order to have positive energy values, we introduce the electronic affinity, noted

AE = -Eatt.

is the energy required to oxidise an anion M- to the elementary atom stage, according to :

$$\mathbf{X}^{-}(\mathbf{g}) \longrightarrow \mathbf{X}^{+}(\mathbf{g}) + \mathbf{e} - \text{Ainsi}, \mathbf{E}\mathbf{A}_{1} = -\mathbf{E}\mathbf{a}\mathbf{t}\mathbf{t}$$

Electron affinity is often expressed in eV (in which case it refers to a single atom), whereas ionisation energy is more often expressed in kJ-mol-1 (in which case it refers to a mole of atoms).

It is essential to know how to convert units:

 $1 \text{ eV} = 1,6 \ 10^{-19} \text{ J}$, the result is expressed in J-mol-1 after multiplication by the AVOGADRO constant $N_A = 6,022 \ .10^{23} \text{ mol}^{-1}$

The electronic affinity varies in the same direction as the ionisation energy

Over a period: if Z ≯ ⇒ EA ≯ *On a column*: if Z ≯ le n ≯ ⇒ EA ↘

In general, the anion formed is more stable than the neutral atom and, in order to maintain positive numbers for the EA, the latter is equal to the opposite of the thermodynamic balance used (reactants -> products).

positive numbers for the AE, this is equal to the opposite of the thermodynamic balance used (reactants -> products). The following table shows the AEs of a few selected atoms

(values in eV).

| Atome | Н | Li | C | N | 0 | F | S | Р | CI | Br |
|-------|------|------|------|------|------|------|------|------|------|------|
| AE | 0,75 | 0,62 | 1,26 | 0,05 | 1,47 | 3,40 | 2,07 | 0,75 | 3,61 | 3,36 |

The table shows two families of elements:

- atoms with low EA (H, Li, N, P);

- those with a high A EA (O, F, S, Cl, Br).

Electronegativity χ (EN)

No unit

The electronegativity of an atom is defined as its ability to attract electrons to itself within a molecule.

Electronegativity represents the ability of an element to attract electrons to itself when it is involved in a covalent bond.

In the Pauling scale, fluorine is by convention the most electronegative element, with $\chi(F) = 4,0$. The least electronegative element is francium $\chi(Fr) = 0,7$





- Let's look at the Mulliken and Pauling definitions of electronegativity, and the consequences that follow from them (ionic nature of a bond and dipole moment).
- > The first definition of electronegativity was given *by Mulliken*.

It is expressed as the average of the first ionisation energy EI1 and the electron affinity AE.

$$\chi = \frac{\mathrm{EI} + \mathrm{AE}}{2}$$

The Pauling scale is based on the difference in binding energies for diatomic molecules.

Pauling suggested that the difference between the electronegativities χ A and χ B of two atoms A and B is given by :

$$|\chi_{A} - \chi_{B}| = 0,208 \sqrt{D_{AB} - \sqrt{D_{AA} - D_{BB}}}$$

where D_{AB} is the binding energy of molecule AB ($kJ. \mbox{ mol-1})$ and

 D_{AA} and D_{BB} are the corresponding values for molecules A_2 and B_2 .

By definition, $\chi_{\rm E} = 4$ and all the others can be deduced from this.

The Allred and Rochow scale can be used to calculate electronegativity using the equation :

where Zeff is the effective charge for an added electron calculated using Slater's method.

Ra is the radius of element A in angstrom.

Using both scales, the electronegativities of the 5 most electronegative elements are :

F (x = 4), O (x = 3, 5), Cl (x = 3, 16), N(x = 3, 04) and Br (x = 2.96).

For the least electronegative elements, we have : Fr and Cs (x = 0.7).

- The lower the ionisation energy, electronegativity and electron affinity, the more metallic the element. Conversely, elements with high ionisation energies, electronegativities and electron affinities are non-metals.
- Non-metals therefore cluster around the top right-hand corner of the table (typically fluorine and chlorine), while the vast majority of elements have a more or less pronounced metallic character, with the most metallic clustering around the bottom left-hand corner (typically francium and caesium). Between these two extremes, we usually distinguish between metals:

- > alkali metals, the most reactive ;
- > alkaline earth metals, which are reactive to a lesser degree than the alkaline earth metals;
- > the lanthanides and actinides, which include all the metals in **block f**;
- transition metals, comprising most of the metals in the d block;
- > poor metals, which include all **the p-block metals**.





Tableau périodique des éléments indiquant leur rayon de covalence expérimental¹¹ en picomètres



Tableau périodique des éléments indiquant leur 1^{re} énergie d'ionisation expérimentale^{13, 14} en eV

| H 2,2 | | | | | | | | | | | | | | | | | | He |
|-------------------|-------------------|----|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|------------------|
| Li 0,98 | Be 1,57 | | | | | | | | | | | | B 2,04 | C 2,55 | N 3,04 | O 3,44 | F 3,98 | Ne |
| Na 0,93 | Mg 1,31 | | | | | | | | | | | | Al 1,61 | Si 1,9 | P 2,19 | S 2,58 | CI 3,16 | Ar |
| K 0,82 | Ca 1 | | Sc 1,36 | Ti 1,54 | V 1,63 | Cr 1,66 | Mn 1,55 | Fe 1,83 | Co 1,88 | Ni 1,91 | Cu 1,9 | Zn 1,65 | Ga 1,81 | Ge 2,01 | As 2,18 | Se 2,55 | Br 2,96 | Kr 3 |
| Rb 0,82 | Sr 0,95 | | Y 1,22 | Zr 1,33 | Nb 1,6 | Mo 2,16 | Tc 1,9 | Ru 2,2 | Rh 2,28 | Pd 2,2 | Ag 1,93 | Cd 1,69 | In 1,78 | Sn 1,96 | Sb 2,05 | Te 2,1 | 2,66 | Xe 2,6 |
| Cs 0,79 | Ba 0,89 | * | Lu 1,27 | Hf 1,3 | Ta 1,5 | W 2,36 | Re 1,9 | Os 2,2 | Ir 2,2 | Pt 2,28 | Au 2,54 | Hg 2 | TI 1,62 | Pb 2,33 | Bi 2,02 | Po 2 | At 2,2 | Rn 2,2 |
| Fr 0,7 | Ra 0,9 | ** | Lr 1,3 | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn | Nh | FI | Мс | Lv | Ts | Og |
| | | Ļ | | | | | | | | | | | | | | | | |
| | | * | La 1,1 | Ce 1,12 | Pr 1,13 | Nd 1,14 | Pm 1,13 | Sm 1,17 | Eu 1,2 | Gd 1,2 | Tb 1,1 | Dy 1,22 | Ho 1,23 | Er 1,24 | Tm 1,25 | Yb 1,1 | | |
| | | ** | Ac 1,1 | Th 1,3 | Pa 1,5 | U 1,38 | Np 1,26 | Pu 1,28 | Am 1,13 | Cm 1,28 | Bk 1,3 | Cf 1,3 | Es 1,3 | Fm 1,3 | Md 1,3 | No 1,3 | | |
| | | | | | | | | | | | | | | | | | | |

Tableau périodique des éléments indiquant leur électronégativité selon l'échelle de Pauling