Periodic trends in atomic, electronic configuration & Shielding

Inorganic Chemistry (2): Che-122

2nd lecture / A

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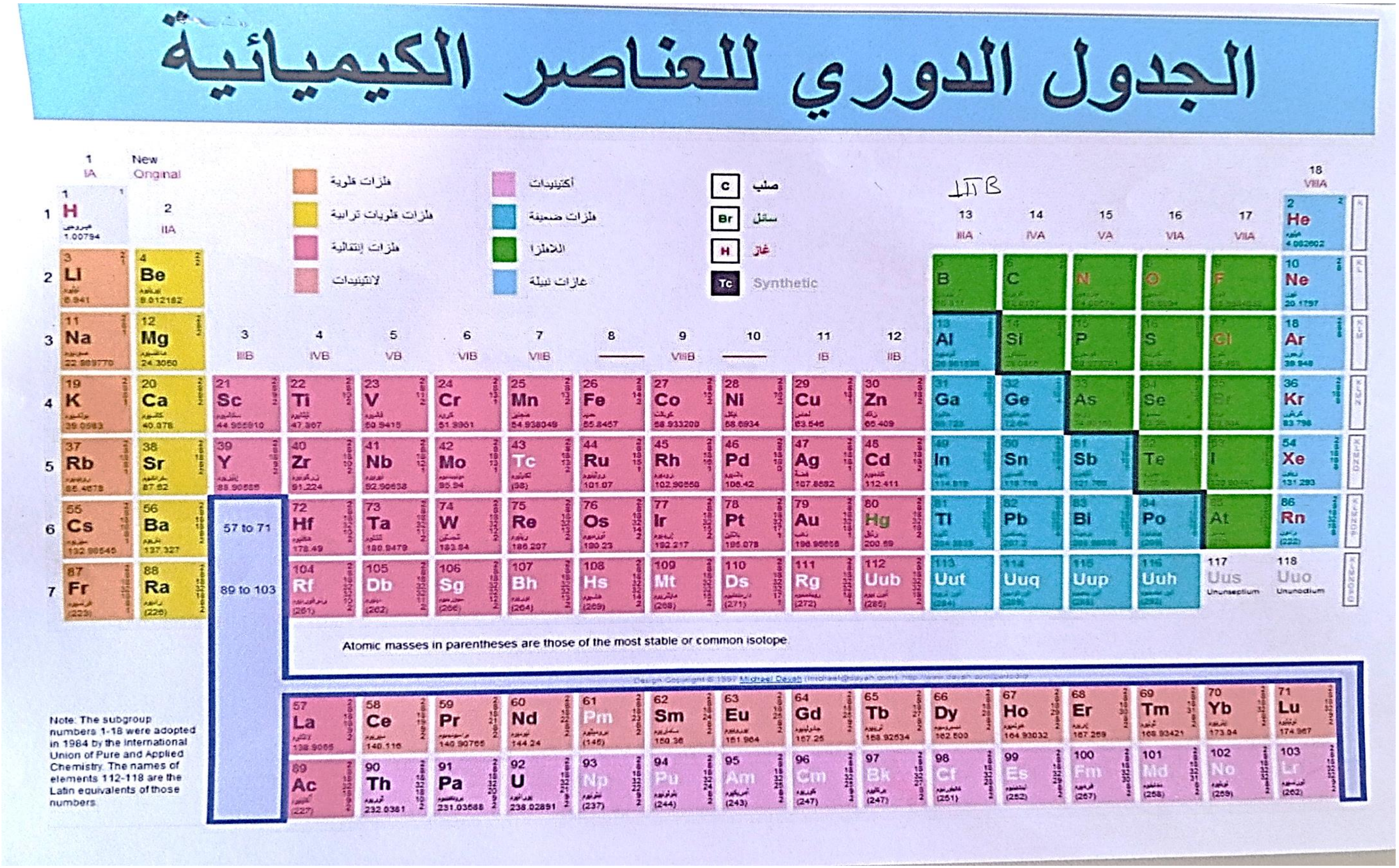
2023-2024


الجدول الدوري للعناصر الكيميائية
فلزات قلوية
فلزات قلويات ترابية
فلزات إنتقالية
لانثنيدات
أكتينيدات
فلزات ضعيفة
اللافلزات
غازات نبيلة
صلب
سائل
غاز
Synthetic
Atomic masses in parentheses are those of the most stable or common isotope
Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.
57 to 71
89 to 103
New
Original

Modern periodic list:

The modern periodic list relies on two characteristics for arranging the elements:

1- Similar characteristics in the elements in the same column (family characteristics).

2- The elements in a row or line are arranged according to atomic number and not according to atomic weight, from smallest to largest.

3- All elements written in **black** are solids at room temperature.

4- All elements written in **red** are liquid elements/substances at room temperature.

5- All elements written in **blue** are gaseous elements/substances at room temperature.

6- All items written in **blank font (white)** are manufactured items.

١- الصفات المتشابهة في العناصر المتواجدة في العمود الواحد (صفات العائلة). وتمثل (المجموعة أو الزمرة).

٢- العناصر في الدور او السطر الواحد ترتب حسب العدد الذري وليس حسب الوزن الذري من الأصغر الى الاكبر. وتمثل (الدورة).

٣- كل العناصر المكتوبة **باللون الاسود** هي عناصر/مواد صلبة في درجة حرارة الغرفة.

٤- كل العناصر المكتوبة **باللون الأحمر** هي عناصر/مواد سائلة في درجة حرارة الغرفة.

٥- كل العناصر المكتوبة **باللون الأزرق** هي عناصر/مواد غازية في درجة حرارة الغرفة.

٦- كل العناصر المكتوبة **بالخط المفرغ (اللون الأبيض)** هي عناصر مصنعة.

Periodic trends in atomic & electronic configuration

General introduction

Inorganic chemistry is concerned with studying the properties of more than a hundred elements in their different states within the periodic table (the number of which has **reached 118** so far) and their compounds and complexes, as well as their applications in various fields that are in direct contact with human life and daily activities. Many attempts have been made to classify elements in different ways, but the most common and widely used is what the scientist Mendeleev arrived at in 1896, according to which he demonstrated that the general properties of elements are related to their electronic configuration and atomic weights.

Mendeleev arranged the elements into vertical groups, in which the elements **have the same number of electrons in their outermost energy orbitals, and into horizontal rotations, in which the elements have the same principal quantum number (n)**.

Electronic Structure and Periodic Table

The periodic table consists of eight main numerical groups (groups, columns) and seven horizontal periods (periods).

1- Short Periods

a- First short periods (n=1)

This period consists of only **two** elements **He_2, H_1** and this period is filled with only two electrons.

b- Second short periods (n=2)

This period consists of **eight** elements and is filled with only eight electrons.

2 nd period = Li(3) → Ne (10).

c- Third short period (n=3)

This period is filled with only **8** electrons, which means that it consists of eight elements.

3 nd period = Na(3) → Ar (18).

2- Long periods

a- first long period or fourth period

This period consists of **18** components.

4 th period = K(19) → Kr (36).

b- Second long period or fifth period

This period consists of **18** components.

5 th period = Rb(37) → Xe (54).

c- Third long period or sixth period

This period consists of **36** components.

6 th period = Cs(55) → Rn (86).

d- Forth long period or 7th period

This period consists of **32** components.

Fr(87) → Ha (105)

"*Main group elements*" (*group and columns*)

The periodic table groups are divided into eight main groups, and at the same time they are divided into two secondary groups or two secondary categories, called group **A** and group **B**. The elements in the periodic table are divided into:

1- Noble gases VIII

These elements are represented by the eighth group (VIII A), also called the zero group elements, as these elements are distinguished by the fact that all their shells are completely filled with electrons and their location is at the far end of the periodic table.

2- Representative elements

These elements have secondary shells that are unsaturated with electrons of the **S** and **P** type, represented by groups, in which the **S** shell is not filled with electrons and these elements behave as metals, while the secondary shell of the P type is not filled with electrons for the group elements, some of which behave as nonmetals and the other part as metalloids.

In other words (it has internal energy levels that may be filled with electrons to their maximum capacity and is divided into two groups [Noble gas] nS^{1-2}.

A- Alkali metals (elements)

B- Alkali earth elements

Because the outer shell is not saturated. If electrons are added to the **S** shell, then the first is called the S-block elements group (alkaline and alkaline earth).

Or a group of pre-transition elements. If the addition to the secondary shell is **P**, then the other is called a group of P-block elements, or post-transition elements.

Alkali earth elements

As for the **third** group, it begins with the element boron **(B)** and ends with the element thallium **(Th).**

As for the **fourth** group, it begins with carbon **(C)** and ends with lead **(Pb).**

As for the **fifth** group, it begins with the element nitrogen **(N)** and ends with the element bismuth **(Bi).**

3- Main Transition Elements

These elements are divided into:

A- First transition elements series.

B- Second transition elements series.

C- Third transition elements series.

These elements are represented by groups **(IB-VIIIB)** that have an outer secondary shell type **(d)** that is not completely filled with electrons. These elements are placed in the middle of the periodic table, and they are all metals.

Inner Transition Elements

The internal transition elements are called F-block elements, these elements have a secondary shell type and consist of **14** elements and their outer shell contains sublevels of the type f, d, S (ns, (n-1)d, (n-2) f) and the **f** orbitals are not filled. It consists of two families or classes: the lanthanes and actinides which are placed at the bottom of the periodic table.

How to write an Electronic Configuration

Basically, **three rules** are required to write a correct electron configuration:-

1- The Aufbau Principle.

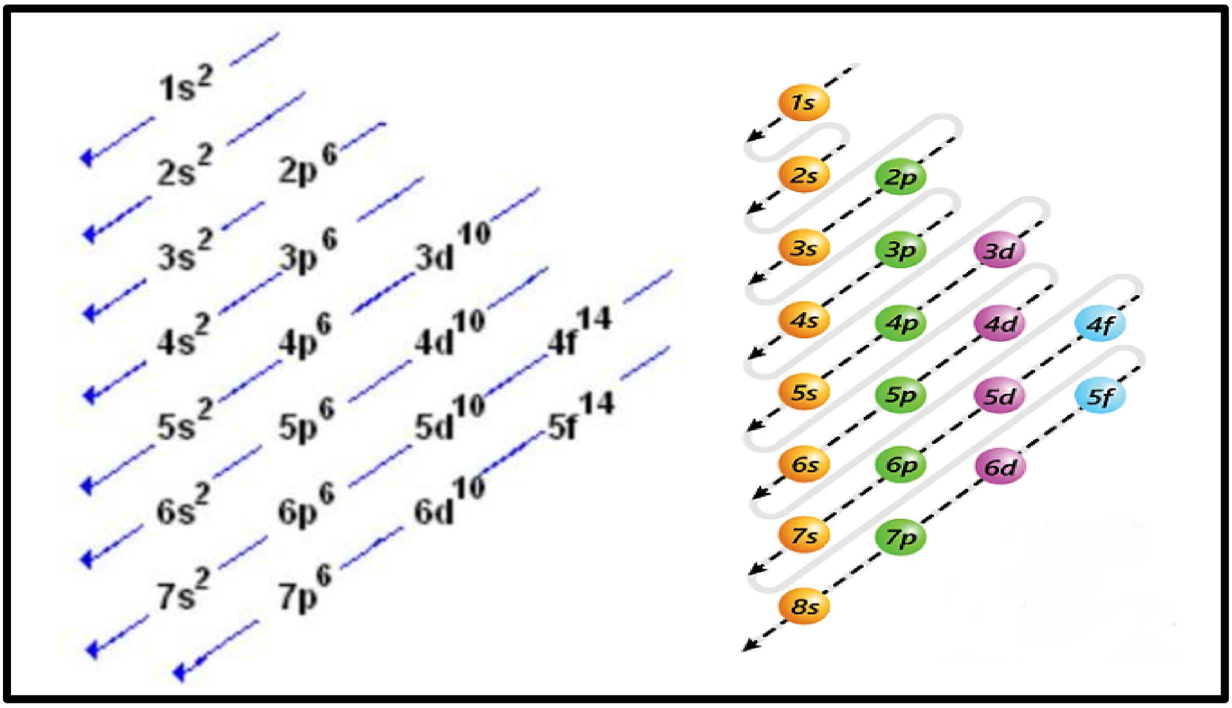
2- Pauli Exclusion Principle.

3- Hund's Rule.

Firstly: Aufbau Principle or the upward construction principle

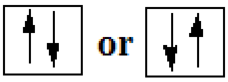
Electrons enter the lower energy sublevels first and then fill the higher ones after that.

Note: The energy of the orbital increases with increasing quantum number. The principal quantum number, often written **n**, represents the energy of the orbital and its distance from the nucleus.



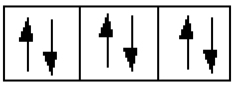
<u>Pauli's Rule:</u> If in the same atom, no two electron can have the same set of quantum numbers

There is only one orbital in the **n=1** quantum shell, from Pauli Exclusion Principle, a maximum of two electrons can be accommodated in it. Using the symbol of **S** orbital with maximum number of electron can be written as $\mathbf{1S^2}$ or $\mathbf{1S}^{\uparrow\downarrow}$ represented box (or square) and arrow as:



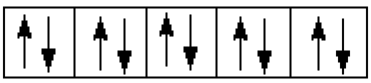
Thus, the three orbitals in a **P** subshell can accommodate six electron, nP^6 (nP_x^2, nP_y^2, nP_z^2) or ($nP_x^{\uparrow\downarrow}$, $nP_y^{\uparrow\downarrow}$, $nP_z^{\uparrow\downarrow}$) or using the Box and arrow as:

p_x p_y p_z

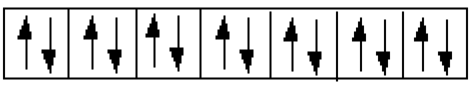


The five and seven orbitals in **d** and **f** subshells can accommodate a total of ten and fourteen electrons respectively:

nd^{10}:



nf^{14}:



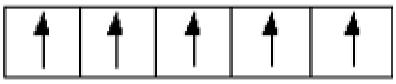
There is one orbital in the quantum shell n=1, according to the Pauli Exclusion Principle, the maximum number of electrons that can occupy or inhabit that single orbital is two electrons.

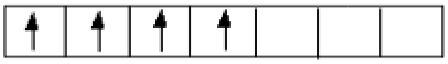
Hund's Rule of Maximum Multiplicity

Hund's rule requires that electrons be distributed unpaired into independent orbitals of equal energy as much as possible.

The reasons that led to the formulation of this rule can be understood by understanding the force of electrostatic repulsion that exists between negatively charged electrons. The repulsion between electrons that occupy different regions of space (or orbitals separated from each other) weakens or decreases, while the electrostatic repulsion between paired electrons that occupy the same space or region of space (i.e., they occupy the same orbital) strengthens or increases.

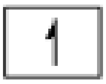
Electron configuration according to Hund's rule:-

nd= 

nf= 

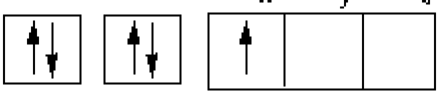
The decrease in electrostatic repulsion between electrons results in a reduction in the energy content of the atom.

Examples of Pauli's Rule & Hund's rule

$_1$H: $1S^1$ 

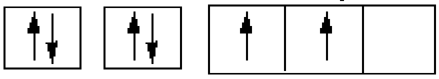
$_5$B : $1S^2$ $2S^2$ $2P^1$

$2P_x$ $2P_y$ $2P_z$



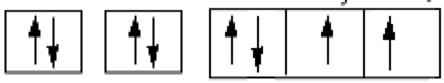
$_6C$: $1S^2$ $2S^2$ $2P^2$

$2P_x$ $2P_y$ $2P_z$



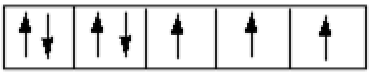
$_8O$: $1S^2$ $2S^2$ $2P^4$

$2P_x$ $2P_y$ $2P_z$



$_{27}Co$: $1S^2$ $2S^2$ $2P^6$ $3S^2$ $3P^6$ $4S^2$ $3d^7$

$3d^2_{xy}$ $3d^2_{xz}$ $3d^1_{yz}$ $3d^1_{x^2y^2}$ $3d^1_{z^2}$



Since the electrons are distributed individually, then the sixth electron is paired, and then the seventh electron is in the **d** orbital.

Covalent electrons

They are the electrons in the outer orbit that participate in the bonding process

If the **outer orbit is saturated**, the atom is stable and chemically inert, as in the inert elements Such as **helium** and **neon**.

If the outermost orbital of the electrons is not saturated, the atom is **unstable** though being **electrically neutral**, it tends **to reach a state of stability** by **granting or gaining.**

Neighboring atoms share valence electrons to reach a saturated state and thus bond atoms with each other.

For **S** section, then the period number = n for the outer shell **S**.
For the **P** section, the period number = n for the outer shell **P** and outer **S**.
For the **S** section, the group number = the number of outer **ns** electrons
For the **p** section, the group number = the number of outer **ns** electrons + the number of outer **np** electrons.

Examples:

The third group results from the collection of **3s, 3p** electrons.

The third group

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

The third period

Group=2+1 the total number of electrons in **S** and **P=3**.

- The **p** section because it ends with the outer p envelope

Examples for determining period and group

- Various examples of identifying the period, group, and section of an element:

Determine the period, group, and section of the element whose atomic number is 9.

- The seventh group results from the addition of valence electrons 5+2.

The seventh group

$\mathbf{1s^2\ 2s^2\ 2p^5}$

The second period

This element is in the second period because it ends with the principal quantum number **2**. It also falls within the seventh group (A VII A) due to the presence of seven electrons in the shell parity it is also located in the **P** section, where the element's valence electrons are located in addition to it ended with section **F.**

Determine the period, group, and sector of the element whose atomic number **(Z)** is:

- **11 Electronic arrangement:**
- **The first group**

First group

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

Third period

This element is located in the **third period** because it ends with a principal quantum number **3**.

It also occurs in the first group (IA): due to the presence of one electron in **3s**. The **S** section is where the valence electron of the element is located where the valence electron is located for the element as well ended with orbital **s**.

Shielding or Screening

If Bohr's laws were reviewed in calculating the speed of the electron.

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

(The energy of the electron in the orbit) $E_n = \frac{2\pi^2 me^4 z^2}{n^2 h^2}$

$$\Delta E = \frac{2\pi^2 me^4 z^2}{h^2}\left(1/n_1^2 - 1/n_2^2\right)$$

$n_2 > n_1$

But if we assume that the electron completely left the atom, then $\mathbf{n_2} = \infty$ and **ΔE** in this case corresponds to the ionization energy.

<u>Ionization energy:</u> It is the least energy required to completely displace or remove an electron from an atom and convert it into a positive ion. This energy is measured in energy units K J $mole^{-1}$, K cal $mole^{-1}$.

1eV= 23.6 K cal.$mole^{-1}$ = 96.49 K J $mole^{-1}$

In the hydrogen atom, the value of **n = 1**, and thus the numerical value of the ionization potential of the hydrogen atom can be found according to the same law.

$$\mathbf{H(g)} \xrightarrow{\mathbf{Ip\ H}} \mathbf{H^+ + e}$$

IpH= 13.6 eV

$$\mathbf{IP} = \frac{2\pi^2\,(1.6x10^{-19})^4 x9.11x10^{-31} (1)^2}{(1)^2 (6.626\,x\,10^{-34})^2}$$

IpLi= IpH x Z^{*2}/ n^2

***Shielding*:** The reduction of true nuclear charge **(Z)** by inner electron or orbitals to the effective nuclear charge (Z*) that experiences by outer electrons or orbitals is called **Shielding** or **Screening**. For a given principle quantum number (n), S orbital is least screened or shielded and has the lowest energy; P, d, and f orbitals have successively higher energy.

→ n=2

∴ ٢S < 2P

→ n=3

∴ 3S < 3P < 3d

→ n=4

∴ 4S < 4P < 4d < 4f

This order is expressed in typical order. Note that there is an exception or departure from this arrangement.

→ **Direction of energy increase**

It was stated above indicates the diversity of the energies of the secondary shells of a particular primary shell in the multi-electron atom [such as $_6C$, $_7N$, $_8O$]. There is no variation in the energies of the secondary shells of excited atoms and hydrogen ions due to the complete lack of blocking in single-electron systems.

Shielding Constant (S)

In general, the ionization potential of the second atom is higher than the ionization potential of the first atom, and the ionization potential of the third atom is higher than the ionization potential of the second atom, but it has been found in practice that the ionization potential of **Li** is **5.7 eV**, i.e. much lower than the ionization potential of hydrogen, and it is the correct value for the following reasons:

1- That the last electron of lithium is located in the **2S** orbital or **n = 2**, and this means that it is farther from the nucleus than the electrons located in the **1S** orbital or **n = 1**, which are closest to the nucleus, so the attraction of the nucleus on the ions of the outer shell located in **2S** is weaker than the attraction of the hydrogen atom. For the outer electron located in **1S**, that is, the energy required to lift the electron is less than the energy required to remove an electron in the hydrogen atom.

2- The nucleus of the lithium atom, which is **Z=3**, is surrounded by two **$1S^2$** electrons revolving around the nucleus, which leads to blocking the charge of the nucleus from the third electron located in **2S1**, meaning that the effect of the charge of the nucleus on the last electron is less than it is with **$2S^1$** electrons, so the nucleus' attraction to this electron is less. The energy required to remove the electron becomes low, and S orbital electrons are generally considered to be the most sensitive to the charge of the nucleus, or in other words more capable of blocking the charge of the nucleus than the rest of the other electrons. Also, the blocking of **1S** electrons is higher than the blocking of **2S** electrons.

$\longleftarrow$ **Increase of shielding**

S > P > d >

1- Increase of sensitivity towards nuclear charge.
2- Increase of attraction toward nuclear charge.
3- Increase of shielding or screening.

This means that what affects the electrons as their atomic number increases is not the total charge of the nucleus **(Z)**, which represents the atomic number, but rather the amount of this charge that reaches the electron and is called the effective charge. We call it Effected nuclear charge, which is the charge that reaches. The electron after some or a percentage of it is blocked by the electrons in the inner shells, that is, after blocking. The effective charge can be calculated from the scientist Slater's equation:

$$Z^* = Z - S$$

<u>Where :</u>

$Z^* = Z - S$.

Z^*= effective nuclear charge.

Z= Total nuclear charge (atomic no.)

S= Shielding or Screening constant.

The Effective Nuclear Charge (Z)*

H is the actual nuclear charge that a particular electron experiences. Effective nuclear charge depends on the numerical values of (n) and (ℓ) of the electron of interest, because electrons in different shells and subshells approach the nucleus to different extents. The effective nuclear charge is sometimes expressed in terms of the true nuclear charge ($\mathcal{Z}$) and an empirical shielding constant ;by the writing:

$$\mathcal{Z}^* = \mathcal{Z} - S$$

Note that the experimental blocking constant varies depending on the secondary shell or the type of orbital.

Shielding increases

←

S >P > d > f

→

Shielding decrease

It can be said that the closer the electron is to the nucleus, the relatively high the effective or actual nuclear charge it senses. The reason for this is due to the diversity of the distances between the various electrons and the nucleus, as well as to blocking by the electrons themselves.

For the purpose of understanding many topics related to the blocking constant, such as atomic size, electronegativity, and ionization energy, the scientist Slater developed a set of preliminary rules to estimate the extent of the approximate blocking of electrons. These rules can be summarized in the following points:

To calculate the blocking constant **S** for an electron located in the **ns** or **np** secondary level, we follow the following steps:

1. The electron configuration of the element is written from left to right according to the following order. This order is called the **Slatter order**.

2. If the electrons that belong to any group are located to the right of the electron for which the blocking constant is to be calculated, they do not contribute to the value of the blocking constant, or in other words, the value of the blocking constant has = **zero**.

3. The electron belongs to the same main shell of the **ns** or **np** type to block the electron for which the blocking constant is to be calculated as **0.35**.
4. Every electron belonging to the **n-1** main shell blocks the electron for which the blocking constant is to be calculated, with an amount of **0.85**.
5. Every electron belonging to the main shell of type **n-2** or less is completely blocked, that is, by an amount = **1**.

a- To calculate the blocking constant for an electron located in the secondary level of the **nd** or **nf** type, all electrons that are located to its left are completely blocked, that is, by one amount, and that are located within the same level. The level is blocked by **0.35**, or in other words, to calculate the blocking constant for an electron located in the secondary level of the **nd** or **nf** type, we use all the previous points except points **4.5**, which become as follows:

All electrons located in the groups to the left of the **nd** or **nf** group block the orbital with its blocking constant by an amount equal to **1**, that is, they are completely blocked.

<u>Example:</u> Calculate the effective nuclear charge for the nuclear charge for the electron no. 64 for the Ac element.

<u>Solution</u>

$_{89}Ac$: $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^6\ 3d^{10}\ 4S^2\ 4P^6\ 4d^{10}\ 4f^{14}\ 5S^2\ 5P^6\ 5d^{10}\ 5f^0\ 6S^2\ 6P^6\ 6d^1\ 6f^0\ 7S^2$

$\underbrace{1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^6\ 3d^{10}}_{n-2}\ \underbrace{4S^2\ 4P^6\ 4d^{10}\ 4f^{14}}_{n-1}\ \underbrace{5S^2\ 5P^2}_{n}$

S= 3x0.35 + 32 x 0.85 +28x1= 44.35

Z*=89-44.35= 44.65.

<u>Example:</u> Find the effective nuclear charge on the last electron in the following elements and ions, $_{7}N$, $_{30}Zn$, $_{51}Sb$, $_{26}Fe^{+2}$, $_{22}Ti^{+2}$, $_{29}Cu^{+}$.

<u>Solution:</u>

$_{7}N$: $\underbrace{1S^2}_{n-1}\ \underbrace{2S^2\ 2P^3}_{n}$

S = (4x 0.35) + (2x 0.85) = 3.1

Z*=7-3.1= 3.9

Zn **(3d)** $1S^2\ (2S\ 2P)^8\ (3S\ 3P)^8$ | $3d^{10}$ | $4S^2$

n-1 n

Z*= 30- 21.15= 8.85

Zn **(4S)** $1S^2\ (2S\ 2P)^8$ | $(3S\ 3P)^8\ 3d^{10}$ | $4S^2$

n-2 n-1 n

Fe^{+2} $1S^2\ (2S\ 2P)^8\ (3S\ 3P)^8$ | $3d^6$ | $4S^0$

n-1 n

S= (5x 0.35) + (18 x1) = 19.75

Z*= 26-19.75= 6.25

Ti^{+2} ?

$_{29}Cu^{+1}$?

- **Which of the following pairs has the highest Ip and why?**

a- Li or Cs

Solution:

$_3Li$: $1S^2\ 2S^1$ S= 0 x 0.35 + 2 x 0.85= 1.7

Z*=Z-S= 3-1.7= 1.3

$Ip_{Li} = Ip_H \times (Z^*)^2/n^2 = 13.6 \times (1.3)^2/ (2)^2$

= 5.7118 eV.

$_{55}Cs$: $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^6\ 3d^{10}\ 4S^2\ 4P^6\ 4d^{10}$ | $5S^2\ 5P^6$ | $6S^1$

n-2 n-1 n

S=0x0.35 + 8x 0.85 +46 x1= 52.3

Z*=Z-S= 55-52.3= 2.7

$Ip_{Cs} = Ip_H \times (Z^*)^2/n^2 = 13.6 \times (2.7)^2/ (6)^2$

= 2.754 eV.

a- b- Li or F ?

b- c- Cs or F ?