

Periodic trends in atomic, electronic configuration & Shielding

Inorganic Chemistry (2)

2nd lecture / B

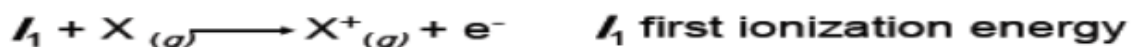
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2023-2024

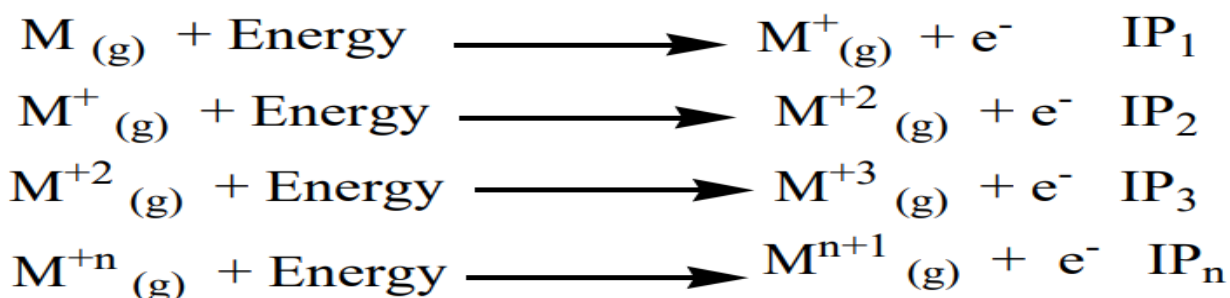
General and periodic properties of the main elements

- **Potential ionization (IP):** It is defined as the lowest energy It is necessary to remove an electron from an atom in the gaseous state. The voltage value increases Ionization, in cycles, by increasing the atomic number due to the decrease in the diameter of the atom, the attractive forces between the nucleus and the valence electrons increase due to the constant quantum number. The main one is to increase the charge of the acting nucleus.
- In the group, the value of the ionization potential decreases with increasing atomic number due to the increase in half diameter, increasing the number of levels, i.e. increasing the principal quantum number and thus reducing the attraction between the nucleus and the outer electrons or valence electrons.
- **Ionization energy:** the minimum energy required to remove an electron from an atom in gas state.
- As for the saturated element, it is very stable, so that the resulting repulsive energy. The amount of pairing of electrons is less than the energy required to dislodge an electron from the valence shell.
- **When comparing the ionization potential of nitrogen and oxygen,** we notice a decrease the value of the ionization potential for oxygen compared to nitrogen due to energy the repulsion that occurs between the extra electron and the half electrons Saturated (couple energy) leads to reduced stability and thus Losing the fourth electron in orbital P is easy, according to... Oxygen, while nitrogen, is half saturated, so it is stable for this reason its ionization energy is high, and the same is the case with beryllium and boron also.

Ionization potential sequence



The ionization energy required to remove one electron from a gaseous atom is called the first ionization energy (IP1). Ionization required to extract the second electron with the second ionization energy (IP2) and so on.



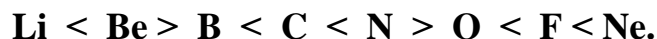
It has been observed that the ionization energy increases according to the following order:

$$\text{IP}_1 < \text{IP}_2 < \text{IP}_3 < \text{IP}_4 \dots\dots \text{IP}_n$$

The value of ionization energy depends on the following factors:

- The amount of effective nuclear charge, which in turn depends on the extent of blocking of other electrons.
- The distance between the electron and the nucleus, or in other words, the length of the most probable radius for this electron.
- The extent of permeability of the electron to the electron cloud to other electrons, as the permeability of electrons decreases in this direction:
S > p > d > f.
- The amount of charge of the positive ion, as the ionization energy increases with the increase in charge of the positive ion.

The following figure gives a simplified explanation that the ionization potential decreases in a single group with an increase in the atomic number, while the ionization potential in a single cycle increases as the atomic number increases as a result of the contraction of the sizes of atoms in a single cycle as a result of the increase in the effective nuclear charge. **with the exception of elements that contain saturated shells or half saturated.**



Determination of Ionization energy

$$E_n = -2\pi^2 m e^4 z^2 / n^2 h^2 \dots \text{ H, He}^+, \text{Li}^{+2}$$

$$E_n = -2\pi^2 m e^4 z^2 / h^2 \dots \text{when } n=1$$

when $z \& n=1$

$$E_n = -2\pi^2 m e^4 / h^2$$

$$\Delta E = IP = 2\pi^2 m e^4 z^2 / n^2 h^2$$

Ionization Energy

- Example.
- Calculate the ionization energy of B^{+4} .
- Ionization energy = 1310 KJ/mol (Z_{eff}^2/n^2)
- So we can measure Z_{eff} .
- The ionization energy for a 1S electron from sodium is.
- 1.39×10^5 KJ/mol.
- The ionization energy for a 3S electron from sodium is.
- 4.95×10^2 KJ/mol.

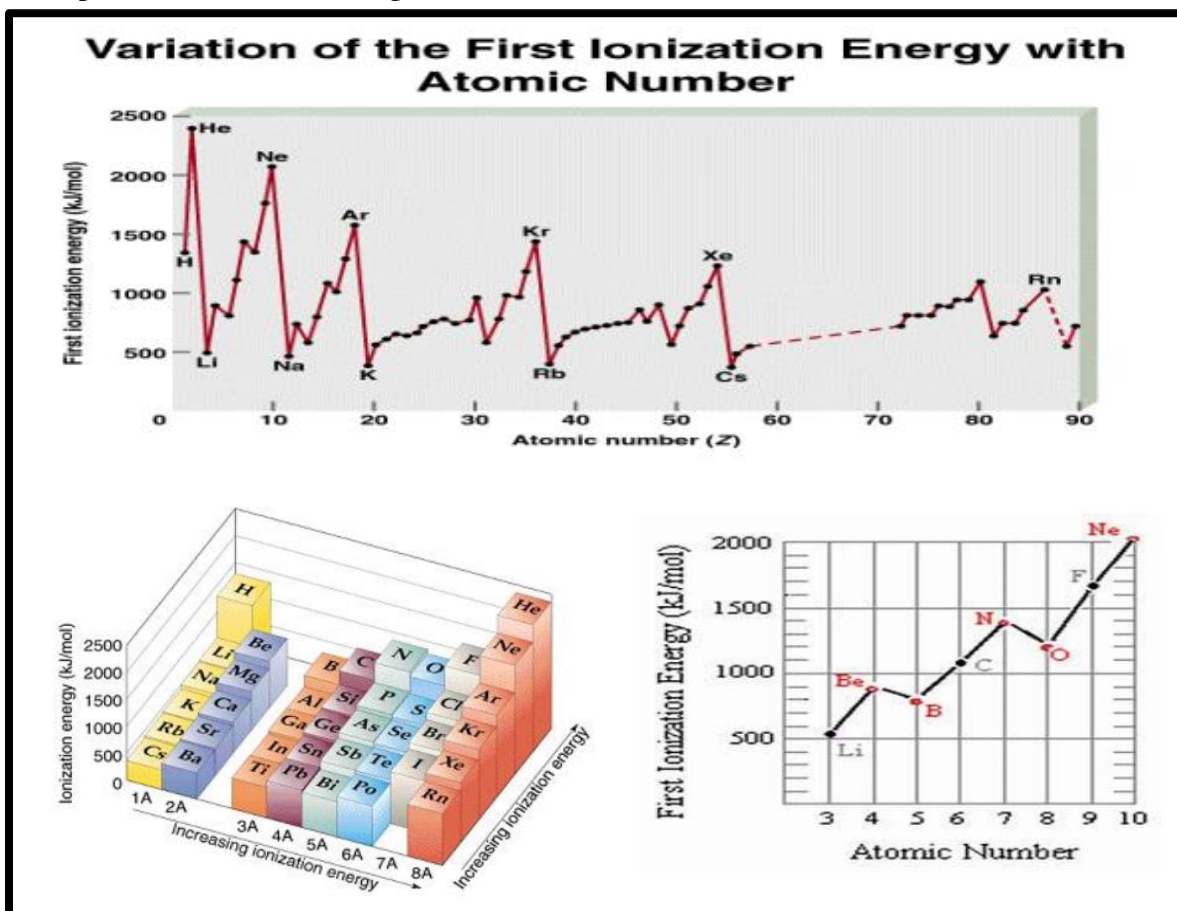
Computed and calculated values of Ground-state, 1st and 2nd ionization energies

Element	Computed values			Experimental values [4]	
	Ground State	1st Ionization energy	2nd Ionization energy	1st Ionization energy	2nd Ionization energy
Hydrogen	-8.4	8.4		13.6	
Helium	-77.64	31.4	46.2	24.6	54.4
Lithium	-183.66	3.4	86.7	5.4	75.6
Beryllium	-388.38	10.9	12.6	9.3	18.2
Boron	-654.16	10.8	25.9	8.3	25.2
Carbon	-1006.82	13.0	16.4	11.3	24.4
Nitrogen	-1455.46	15.9	23.6	14.5	29.6
Oxygen	-2008.56	16.1	31.4	13.6	35.1
Fluorine	-2676.80	23.2	40.0	17.4	34.9
Neon	-3470.44	31.1	49.2	21.6	40.9

Computed and calculated effective nuclear charge of the first ten elements of the periodic table

Element	Atomic number, Z	Effective nuclear charge Z^* (Computed)	Effective nuclear charge [5]
Hydrogen	1	0.849	1
Helium	2	1.844	1.6875
Lithium	3	2.937	2.9606
Beryllium	4	3.538	3.6848
Boron	5	4.39	4.6795
Carbon	6	5.135	5.6727
Nitrogen	7	5.877	6.6651
Oxygen	8	6.614	7.6579
Fluorine	9	7.351	8.6501
Neon	10	8.084	9.6421

The first ionization potential varies with atomic numbers:



Electron Affinity (EA)

It is defined as the change in energy as a result of the atom (in the gaseous state) gaining an electron to form an ion this energy is equal to the ionization energy of the resulting negative ion.



- i- Its value increases in one cycle from left to right, and the reason is that electrons are easily attracted towards nucleation means an increase in the effective charge of the nucleus due to the tendency of atoms to fill their orbitals with electrons.
- ii- The electronic affinity values in each group (group) decrease from top to bottom because electrons the outermost orbitals are less connected because the acting nucleus charge is less due to the increase in number Envelopes, i.e. the principal quantum number.
- iii- Halogens have the highest value of electronic affinity, and the reason is that they lack one electron to reach to place inert elements, as their effective charge is high and their volume is small.
- The electron affinity energy (**EA**) for the nitrogen group is also small because it has a half shell it is saturated, which leads to repulsion between the gained electron and the electrons in the **P** shell.

In one period ${}_{9}\text{F} > {}_{8}\text{O} > {}_{7}\text{N} > {}_{6}\text{C} > {}_{5}\text{B}$
←
Electron affinity increased

In one group ${}_{3}\text{Li} > {}_{11}\text{Na} > {}_{19}\text{K} > {}_{37}\text{Rb}$
←
Electron affinity increased

Always the energy of familiarity first EA Negative sign: any emitter of heat other than elements Noble elements and elements of the second group IIA due to the saturation of their outer shell.

The second and third electron affinities are positive in sign, i.e. endothermic because of the repulsion that occurs between the added electron and the negative ion.



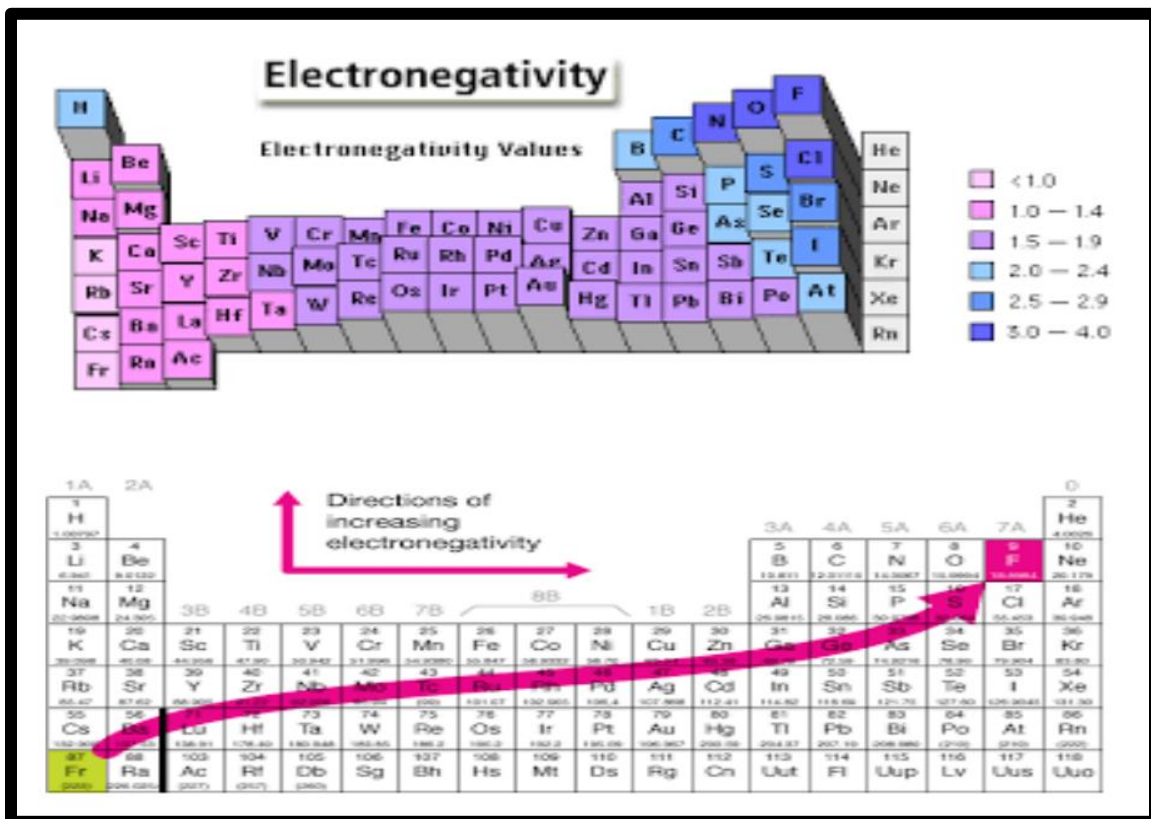
- The value of electron affinity is always less than the value of electronegativity for the element itself because adding an electron to a neutral atom frees up less energy than that added to the positive ion.
- The electronic affinity of the nitrogen γN group elements low because they have semi-saturated shells, which leads to repulsion the gained electron and the electrons in the shell **np** single.

Electronegativity

- **Electronegativity EN: It is a measure of the tendency of an atom in a molecule to attract electrons towards it in the chemical bond.**
- Electronegativity increases in spins, with increasing atomic number, due to decreasing radius the atom, the increase in the acting nucleus charge, and the forces of attraction as a result of the principal quantum number being constant and increasing number of electrons. Electronegativity decreases in the group due to the increase in atomic number, as a result to increase the radius of the atom, and reduce the forces of attraction between the nucleus and electrons the highest electronegativity is the group of halogens, specifically fluorine **F**. The tendency of the element increases gaining electrons, especially halogens, to saturate their outer shell, while the negativity decreases electronegativity of alkaline and alkaline earth elements because they tend to lose electrons to reach the saturated ranking.

- The least electronegative element in the periodic table is cesium Cs.
 ${}_{11}\text{Na} < {}_{12}\text{Mg} < {}_{13}\text{Al} < {}_{14}\text{Si} < {}_{15}\text{P}$

$\xrightarrow{\hspace{10em}}$
Increased of Electronegativity



If the difference in electronegativity between the two bonded atoms in a molecule is large, then the bond formed between them has an ionic character, and if the difference is small in electronegativity, the bond formed between them is covalent.

How to calculate electronegativity

1- Mulliken Method.

- It is considered the oldest method of calculating electronegativity, which is based on the idea. The electronegativity **EN** of an element is the average of two energies (Ionization energy (IP) and electron affinity energy (EA)) according to the following relationship:

$$\text{EN} = 1/2(\text{IP} + \text{EA})$$

Where **EA**, **IP** and **EN** represent the atom in its valence state and not in its valence state the single. Since the valence state of the atom varies with different molecules in which the atom is included, the electronegativity values of the atom in question the calculation by Mulliken's method varies from one molecule to another.

Ex: The I.E. of Be is more than that of B though the nuclear charge of boron atom ($Z=5$) is greater than that of beryllium atom ($Z=4$). This can be explained as follows:

Boron atom ($Z=5$, $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$) is having one unpaired electron in the 2p-subshell. **Be-atom** ($Z=4$, $1s^2 2s^2$) is having paired electrons in the 2s-subshell.

As the fully filled 2s-subshell in **Be-atom** is more stable than **B-atom** due to symmetry. More energy would be needed to remove an electron from **Be-atom**. Hence, **Be** has high I.E.

2- Pauling method

- This method is the most widely applied because it relies on the energy of covalent bonds between two combined atoms **A-B**. The bond energy is represented by the symbol **D_{AB}**, which is higher than the energy of the joint

calculated on the basis of the arithmetic average or the geometric mean of the bonds **B-B**, **A-A**, which are symbolized by **D_{AA}**, **D_{BB}**.

- If we use the arithmetic average, the axis energy equation **D_{AB}** can be written

As follows:

$$D_{AB} = 1/2[D_{AA} + D_{BB}] + \Delta_{AB}$$

- Where Δ_{AB} represents the ionic resonance energy, as Pauling called it, and it increases the greater the difference in electronegativity between the two atoms involved in bond formation.
- By studying a large number of diatomic molecules, Pauling showed that it is possible calculate the energy Δ_{AB} from the following equation:

$$\Delta_{AB} = 23.06(EN_A - EN_B)^2 \quad \text{by eV unit.}$$

It can be written as:

$$EN_A - EN_B = 0.208\sqrt{\Delta_{AB}}$$

Where **EN_A** is the electronegativity of atom **A**

EN_B Electronegativity of the atom **B**.

There is a relationship between the EN values of the elements measured by Pauling's method EN_P It is measured by Mulliken's EN_M method:

$$EN_P = 0.336 (EN_M - 0.615)$$

The following example shows how to calculate Δ_{AB} in a molecule **ClF** using the mean method.

$$D_{Cl-Cl} = 57.3 \text{ kcal.mol}^{-1}$$

$$D_{F-F} = 37.0 \text{ kcal.mol}^{-1}$$

$$D_{Cl-F} = 47.2 \text{ kcal.mol}^{-1} \quad \text{theoretically}$$

$$D_{Cl-F} = 59.5 \text{ kcal.mol}^{-1} \quad \text{practically}$$

By application as follows:

$$D_{AB} = 1/2[D_{AA} + D_{BB}] + \Delta_{AB}$$

$$D_{Cl-F} = 1/2[D_{Cl-Cl} + D_{F-F}] + \Delta_{Cl-F}$$

$$59.5 = 1/2[57.3 + 37.0] + \Delta_{Cl-F}$$

$$\Delta_{Cl-F} = 12.3 \text{ kcal.mol}^{-1}$$

Radii

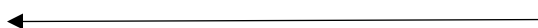
A- Atomic radii

Atomic radius (n): is the distance between the centers of the nucleus the last outer shell of the atom can be designated as the atom by X-ray diffraction and spectroscopic methods. it was found that many physical properties, such as density, boiling point, and melting point, are related to the sizes of atoms, and since it is not possible to isolate atoms as single atoms, the atomic radius was measured indirectly by measuring the distance between the nuclei of two atoms bonded together in gas molecules or between the nuclei of two ions in gas molecules. Solid state (crystal).

It has been observed that the atomic radius increases with the increase in the atomic number of the elements of one group as we move from top to bottom due to the increase in the number of secondary shells, while the atomic radius in one group decreases with the increase in the atomic number, that is, as we move from left to right due to the increase in the nuclear charge affecting the molecules. In which the number of secondary shells remains constant.

And the elements of the periodic table.

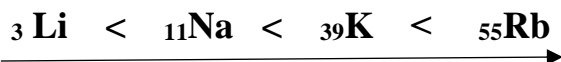
- 1- The radius of the elements of one period decreases as the atomic number increases because of the steady increase in Z^* while the value of n is constant.



The radius increases

- 2- The n of elements in one group increases with increasing atomic number this is because the number of shells increases, meaning the main quantum

number increases the nucleus's attraction to electrons decreases, and the size increases.

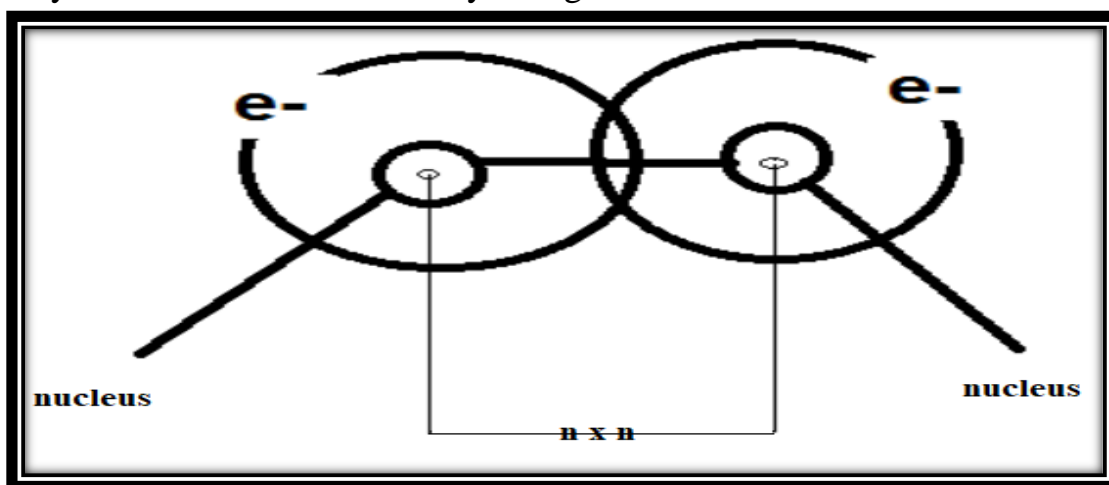


→
The radius increases

- 3- A sudden increase in atomic purity occurs whenever a new cycle begins Periodic table because a new period means **n** increases by **1**.

B-Covalent radii

Covalent radius: It is half the distance between the nuclei of two atoms they are similar to each other by a single covalent bond.



This means that the first atom's electron contributes the same amount as it contributes an electron to the second atom to form the covalent bond, i.e the effect of the two nuclei is a mutual and equal effect on the two electrons. The covalent radius is measured by X-ray diffraction Spectroscopic methods have shown these studies.

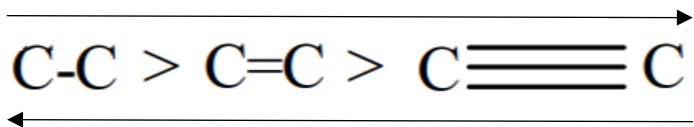
- 1- The covalent radius of an element remains constant throughout compounds.

Example: The C-C bond has a constant length in all compounds and is equal

1.5 Å, so the covalent radii equals to **(0.77) Å**. Such as CH₃-CH₃.

The covalent radius (r) decreases with increasing bond order between two similar atoms.

Decrease of the covalent radius



Increases the length of bond

Ionic radius

In ionic compounds, the radius is measured by diffraction X-rays and the ionic bond is the distance between the two nuclei two ions in contact, one positively charged and the other negatively charged.

$$r_0 = r_a + r_c$$

r_a = anion radii

r_c = cation radii

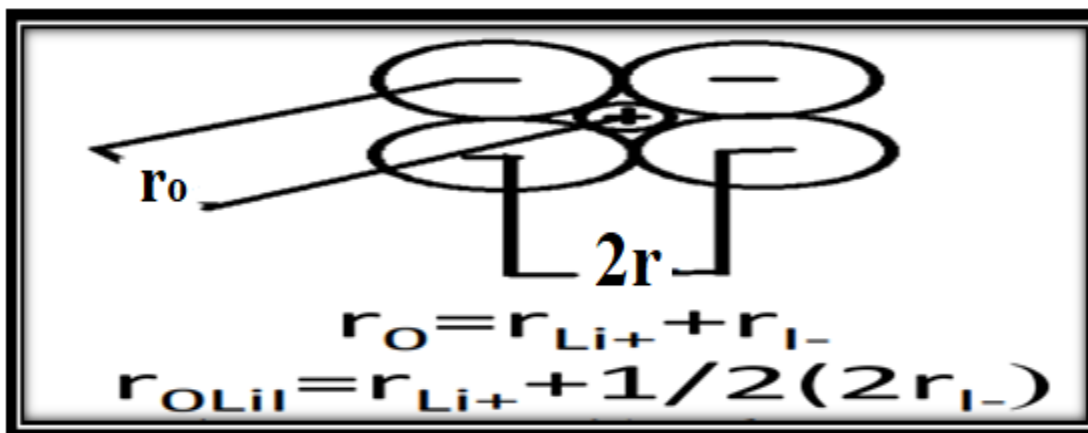
Methods for calculating ionic radius

- 1- Landy method
- 2- Braque's method

Landy method

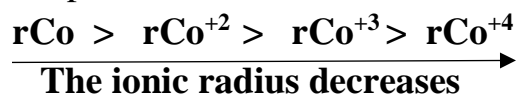
- The scientist has studied lithium halide LiX, where X= F, Cl, Br, and I.

Considering that the positive lithium ion is the smallest ion the positive size is such that it does not prevent contact with the negative halide ions the large charge can therefore be considered half the distance between an examples is the iodide ion nucleus. It is equal to the nucleotide ion Iodide. Using this method, Landy found that the radii for negative iodide ion is **2.13 Å°**.

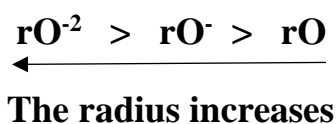


After calculating the radius of F^- ion, Landy was able to calculate $r^- r^+$, for ions Fluorine, chlorine, bromine, sodium, potassium and rubidium.

- Ionic radius increases with increasing atomic number in group or in once group due to increased shielding resulting from the increased number of main shells and dimensions of the effect of nuclear charge on electrons.
- The ionic radius decreases as the oxidation number increases, i.e. as the number increases electrons lost due to increased positive charge density and increased the effective charge of the nucleus, which increases the attraction of the nucleus to the electrons and thus decreases the radius of the positive ion.



The radius of a negative ion is larger than the radius of an atom neutral.



In ions with similar electronic configuration, it is reduced by half the diameter increases as the atomic number of the ion or atom increases.



Each of them has the same electronic configuration.

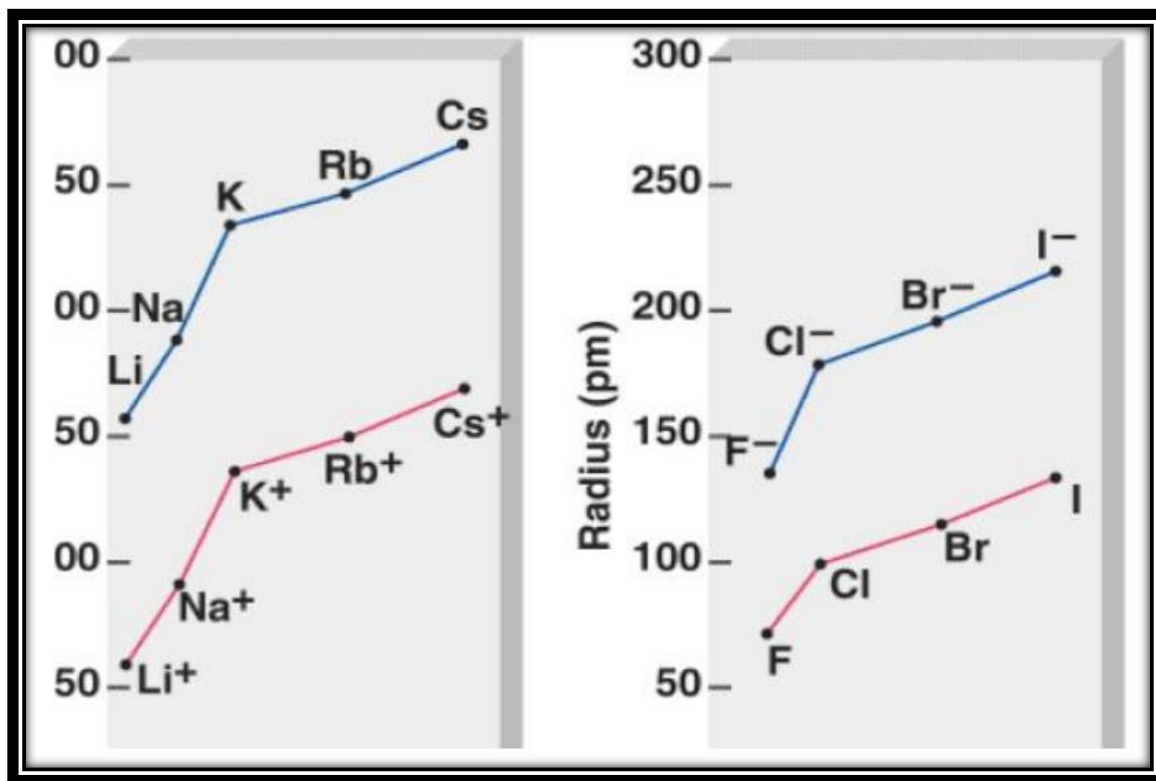


This can be explained by return to the relationship $*Z = Z - S$

Where S is the shielding constant and is equal for all ions and atoms above, because it contains the same number of electrons, and the variable remains the same Atomic number Z : As the atomic number increases, the effective charge of the nucleus increases and decreases Radius (r).

Note: The radius decreases with the increase in the charge of the nucleus acting with fixed of shielding constant.

Comparison between the atomic and ionic radii:



a- Homonuclear Diatomic Molecules:

In case of homonuclear diatomic molecules of A_2 type (e.g. F_2 , Cl_2 , Br_2 , I_2etc). The bond length, d (A-A) is given by:

$$d(A-A) = r(A) + r(A)$$

$$d(A-A) = 2 \times r(A)$$

$$r(\text{A}) = \frac{d(\text{A}-\text{A})}{2}$$

The above equation shows that in the case of homonuclear diatomic molecules of **A₂** type. The covalent radius of an atom **A**, $r(\text{A})$ is equal to one half of the internuclear distance, $d(\text{A}-\text{A})$. Therefore, the covalent radius of an atom in a homonuclear diatomic molecules can be obtained by divided the internuclear distance by two.

Examples:

1. Cl₂ molecules

The value of Cl-Cl bond distance as found experimentally is 1.98 Å°. Thus:

$$r(\text{Cl}) = \frac{d(\text{Cl}-\text{Cl})}{2} = \frac{1.98}{2} = 0.99 \text{ Å}^\circ$$

2. Diamond

The value of d(C-C) distance as found experimentally in a variety of structured hydrocarbons is 1.54 Å°. Thus:

$$r(\text{C}) = \frac{d(\text{C}-\text{C})}{2} = \frac{1.54}{2} = 0.77 \text{ Å}^\circ$$

b- Heteronuclear Diatomic Molecules:

In case of heteronuclear diatomic molecules of **AB** type. bond length, $d(\text{A}-\text{B})$ is given by:

$$d(\text{A}-\text{B}) = r(\text{A}) + r(\text{B})$$

$r(\text{A})$ and $r(\text{B})$ are the covalent radii of **A** and **B** atoms.

Examples:

1. CCl₄ molecules

The experimentally value of $d(\text{C-Cl})$ is 1.76 \AA . Thus:

$$\begin{aligned} d(\text{C-Cl}) &= r(\text{C}) + r(\text{Cl}) \\ r(\text{C}) &= d(\text{C-Cl}) - r(\text{Cl}) \\ &= 1.76 - r(\text{Cl}) \end{aligned}$$

Thus the covalent radius of carbon atom can be calculated by subtracting the covalent radius of **Cl** atom from $d(\text{C-Cl})$ bond length. The covalent radius of **Cl** atom can also be obtained. Provided that covalent radius of **C** atom is known.

2. SiC

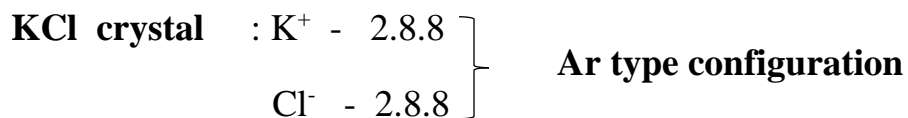
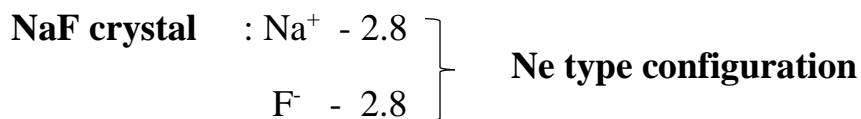
The experimentally value of $d(\text{Si-C})$ is 1.93 \AA . Thus:

$$d(\text{Si-C}) = r(\text{Si}) + r(\text{C})$$

Calculation of ionic radii

Pauling's method

Pauling has calculated the radii of the ions on the basis of the observed internuclear distance in four crystals namely **NaF**, **KCl**, **RbBr** and **CsI**. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.



Further the following two assumptions are made to assign the ionic radii.

- i. The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

$$r(C^+) + r(A^-) = d(C^+ - A^-) \quad \text{----- (1)}$$

Where:

$r(C^+)$ - radius of cation C^+

$r(A^-)$ - radius of anion A^-

$d(C^+ - A^-)$ - internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal.

- ii. For a given noble gas configuration, the radius of ion is inversely proportional to its effective nuclear charge i.e.

$$r(C^+) \propto 1 / Z^*(C^+) \quad \text{----- (2)}$$

$$r(A^-) \propto 1 / Z^*(A^-) \quad \text{----- (3)}$$

Where:

$Z^*(C^+)$ & $Z^*(A^-)$ are the effective nuclear charge of cation (C^+) and anion (A^-) respectively, on combining (2) & (3).

$$r(C^+) / r(A^-) = Z^*(A^-) / Z^*(C^+) \quad \text{----- (4)}$$

Hence the above two equations (1) & (4) can be used to evaluate the values of $r(C^+)$ and $r(A^-)$ provided that the value of $d(C^+ - A^-)$, $Z^*(C^+)$ & $Z^*(A^-)$ are known.

Example:

Calculate the ionic radii of K^+ and Cl^- ions in KCl crystal. The internuclear distance between K^+ and Cl^- ions are found to be 3.14 \AA .

Solution:

$$r(K^+) + r(Cl^-) = d(K^+ - Cl^-) = 3.14 \text{ \AA}$$

K^+ and Cl^- ions have $Ar(Z=18)$ type configuration. The effective nuclear charge for K^+ and Cl^- can be calculated as follows.

$$K^+ = (1s^2) \quad (2s^2 2p^6) \quad (3s^2 3p^6)$$

Innershell (n-1)th shell nth shell

$$Z^*(K^+) = Z - S$$

$$= 19 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]$$

$$= 19 - 11.25 = 7.75$$

$$Z^*(\text{Cl}^-) = 17 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)] \\ = 17 - 11.25 = 5.75$$

$$\therefore r(\text{K}^+) / r(\text{Cl}^-) = Z^*(\text{Cl}^-) / Z^*(\text{K}^+) = 5.75 / 7.75 = 0.74$$

$$\therefore r(\text{K}^+) = 0.74 r(\text{Cl}^-)$$

Substitution (2) in (1)

$$0.74 r(\text{Cl}^-) + r(\text{Cl}^-) = 3.14 \text{ \AA}$$

$$1.74 r(\text{Cl}^-) = 3.14 \text{ \AA}$$

$$r(\text{Cl}^-) = 3.14 \text{ \AA} / 1.74 = 1.81 \text{ \AA}$$