Periodic Table

Effective nuclear charge

The **effective nuclear charge** is the actual amount of positive (nuclear) charge experienced by an electron in a polyelectronic atom.

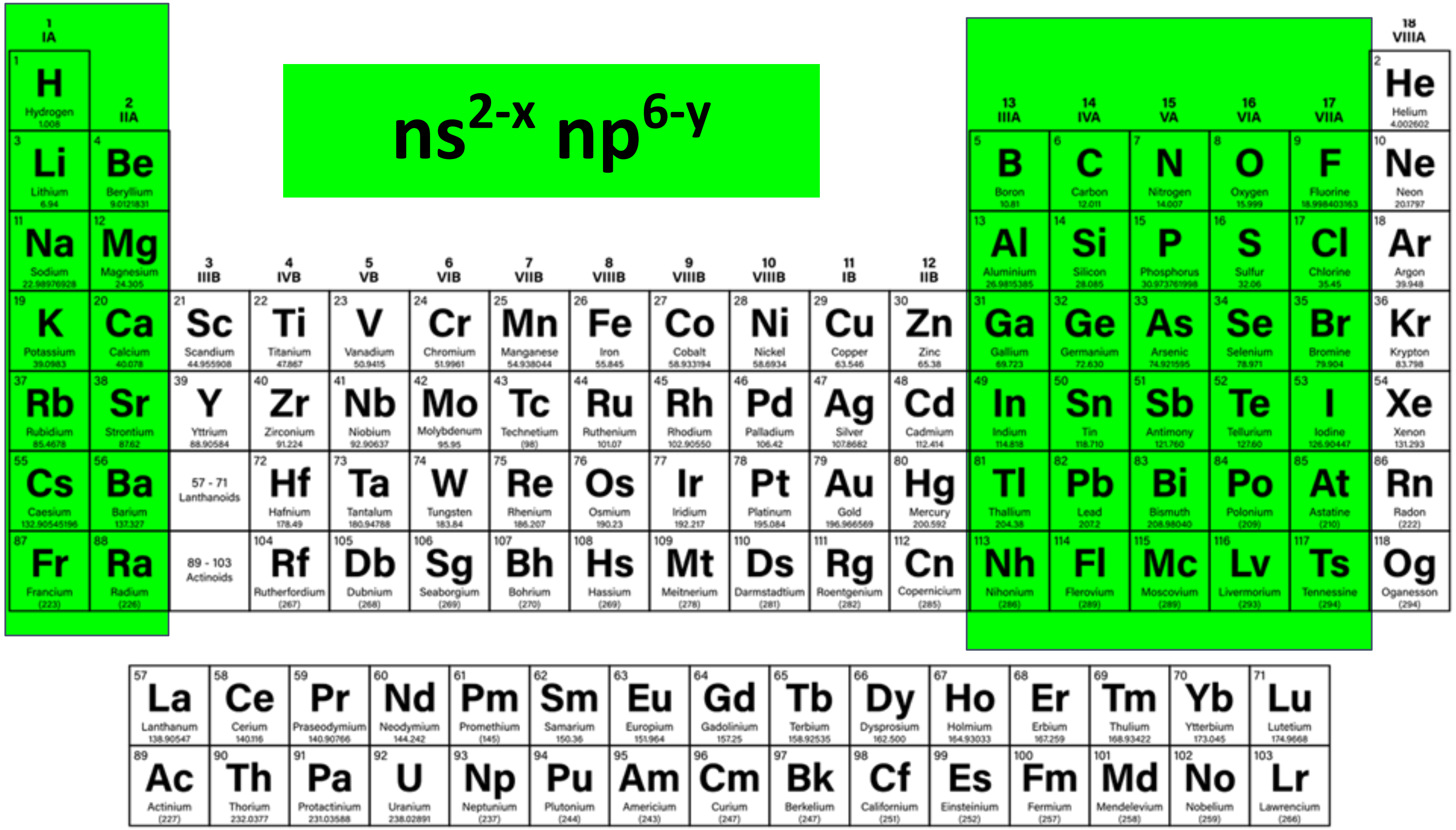
The term "effective" is used because the shielding effect of negatively charged electrons prevent higher orbitals from experiencing the full nuclear charge of the nucleus.

The main group elements

s block element

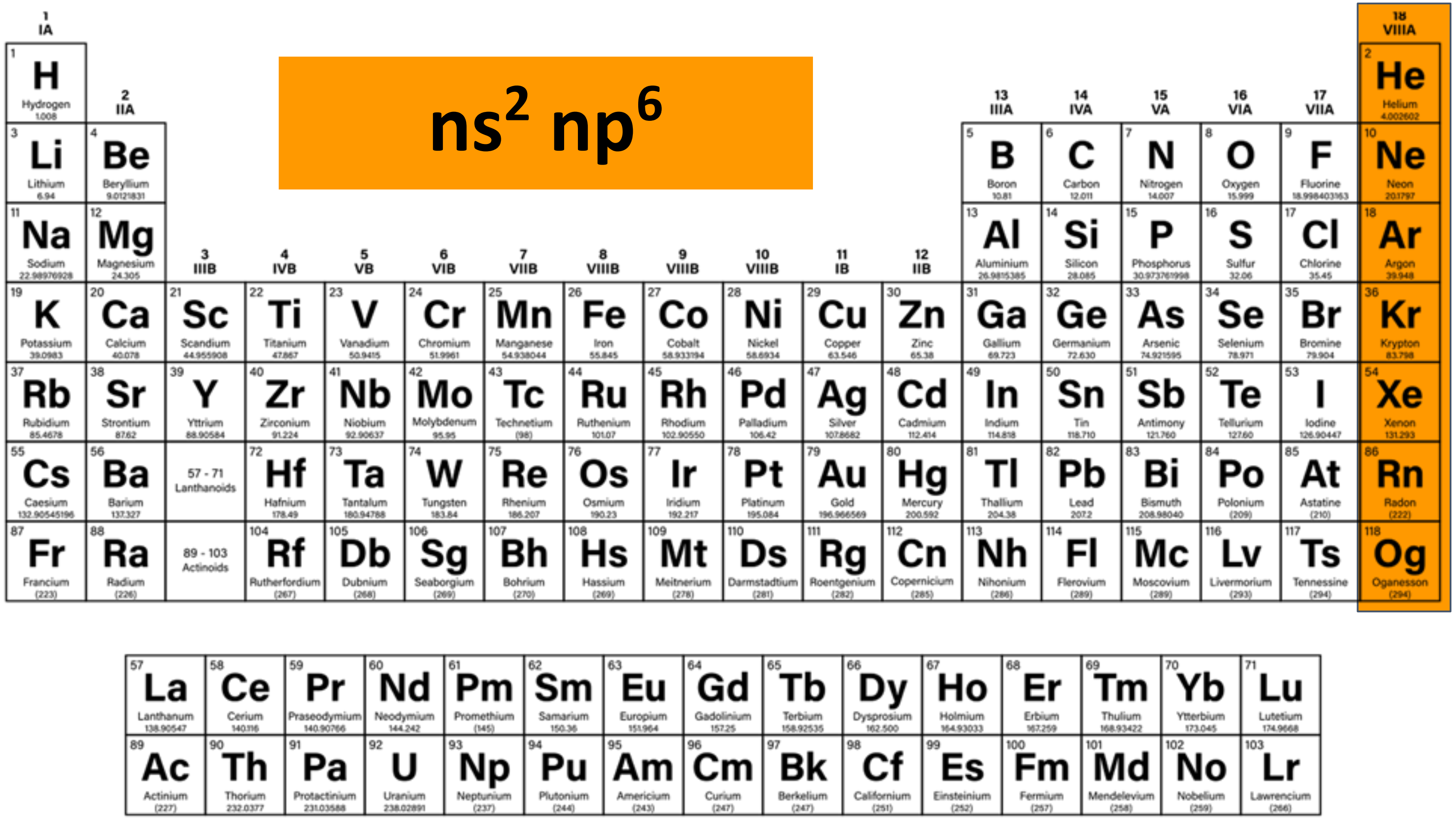
p block element

$$ns^{2-x}\ np^{6-y}$$



The noble family

$ns^2\ np^6$



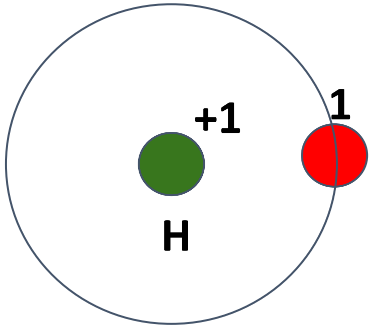
Effective nuclear charge : Slater's rule

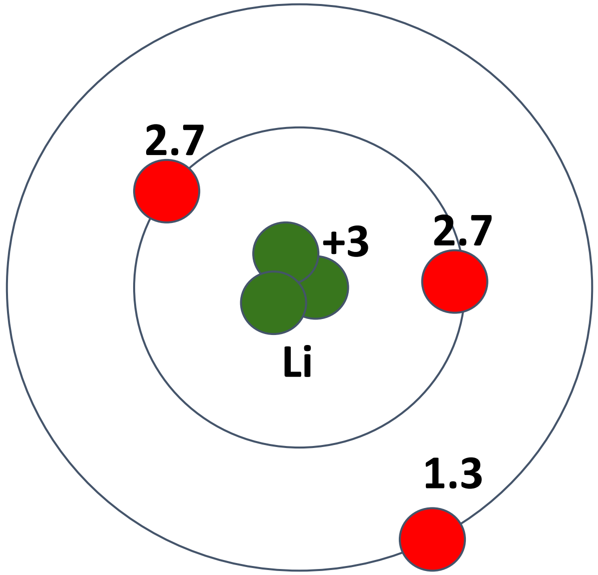
In a multi-electronic system, **effective nuclear charge (Z_{eff})** is the amount of net charge experienced by any individual electron, which is always less than actual nuclear charge (Z).

$$Z_{eff} = Z - \sigma$$

σ = shielding constant

Z_{eff} depends on distance from the nucleus. Closer electrons feel comparatively higher Z_{eff} than distant electrons.





Rules for calculation of σ

Electrons in same group:
Each other electron in the same group, i.e., ns, np, nd or nf-electrons contribute 0.35 to σ (except 1s-electron for which σ=0.3).

Electrons in lower group:
For *s* or *p* subshell, all electrons in next lower shell (n - 1) contribute 0.85 and all electrons in even lower shells (n-2) contribute 1.0 to σ.

For n*d* or n*f* subshell, every electron in groups to the lower contributes 1.0 to σ.

- **Exercise**: Calculate Z_{eff} for Na^+.

Qn. **Calculate the effective nuclear charge for (i) 3p electron in Sulphur, (ii) 4s electron in K?**

Ans: (i) S (16) = 1s2 2s2 2p6 3s2 3p4

$\sigma = (5x0.35) + (8x0.85) + (2x1)$

$= 10.55$

$Z_{eff} = Z - \sigma$

$= 16 - 10.55$

$= 5.45$

(ii) K (19) = 1s2 2s2 2p6 3s2 3p6 4s1

For 4s1, $\sigma = (8x0.85) + (10x1)$

$= 16.8$

$Z_{eff} = Z - \sigma$

$= 19 - 16.8$

$= 2.2$

For F- ion: 1s2 2s2 2p6

$\sigma = 7x0.35 + 2x0.85$

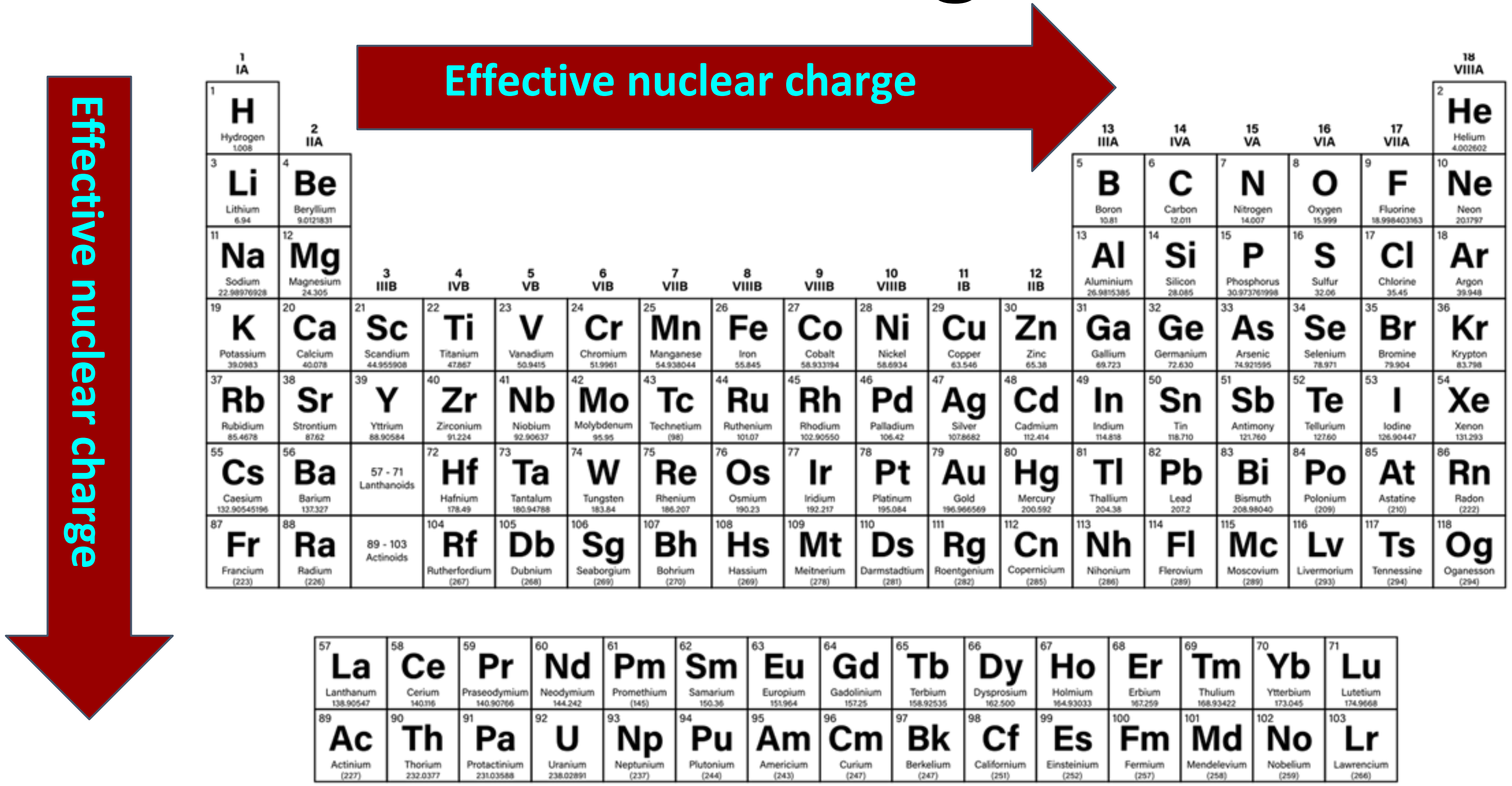
$= 2.45 + 1.70$

$= 4.15$

Effective nuclear charge = 9-4.15

= 4.85

Periodic trends : Effective nuclear charge



Penetration of orbital

Penetration of orbital is defined as the proximity to which an electron can come near the nucleus.
In a multi-electronic system, it is measured by the relative density of electrons (probability density) close to the nucleus.

If shell value (n) is same, then the penetration of an electron follows the following trend in subshells (m_l):

$$s>p>d>f$$

For different values of shell and subshell, it follows the trend:

$$1s>2s>2p>3s>3p>4s>3d>4p>5s>4d>5p>6s>4f....$$

which is also the exact reverse trend for the energy of the electrons.

Variations of s, p, d and f orbital energies in the periodic table

For single-electron system **(H, He^+):**

- Ground state has the least energy than the excited states.
- The energy is decided by the principal quantum number
- If the principal quantum number (n) is same, then all the the orbitals become degenerate.

For multi-electron system:

- The energy is decided by the principal quantum number as well as the azimuthal quantum number (n + l).
- If (n + l) is same then higher n has higher energy value.
- Orbitals experiencing higher shielding effect has higher energy.

Exercise: 3d and 4s which has the higher energy and why?
4p and 5s which has the higher energy and why?

Periodic properties : Electronic configurations

Electrons occupy the orbitals following these 3 principles,

Aufbau principle:

Electrons fill in the orbitals following the order of increasing energy, which means the lowest energy orbitals are occupied first and then the higher energy orbitals.

1s---2s---2p---3s---3p---4s---3d---4p---5s---4d---5p---6s---4f

Hund's rule:

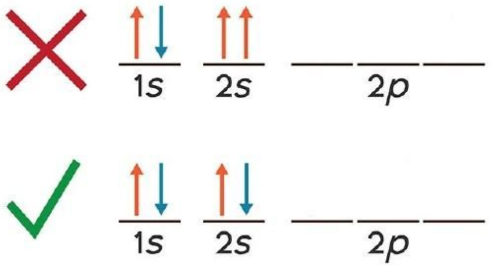
Pairing of electrons are possible only when all other degenerate orbitals are singly occupied.

Dt. 16/11/2021

Electronic configurations

<u>Pauli's exclusion principle:</u>

In an atom or molecule, no two electrons can have all 4 quantum numbers same.



Consider the following pairs

$_{23}V$ ---- $4s^2\ 3d^3$

$_{24}Cr$ ---- $4s^1\ 3d^5$

$_{25}Mn$ ---- $4s^2\ 3d^5$

$_{28}Ni$ ---- $4s^2\ 3d^8$

$_{29}Cu$ ---- $4s^1\ 3d^{10}$

$_{30}Zn$ ---- $4s^2\ 3d^{10}$

Atomic and ionic radius

- For metals (Left hand side of the periodic table, for example Group I, II, IIIA), they loose electron to become +ve cations, and the size of their cation always decreases as the outermost shell is emptied after electron donation.

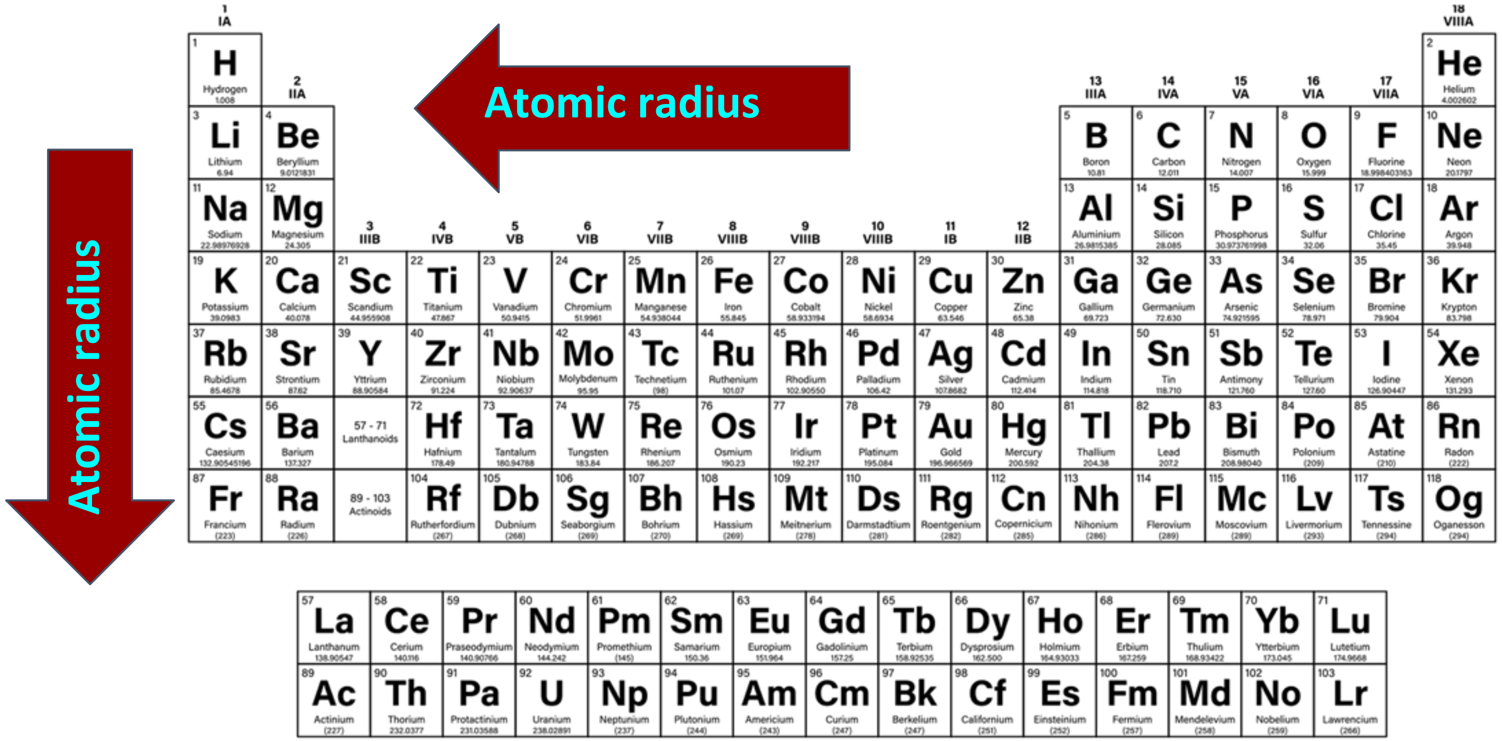
- Moreover, in cation the number of proton is higher than the number of electron as compared to neutral atom, as a result nuclear attraction is more effective.

- Along the period, the atomic and cationic sizes decreases as a result of increasing effective nuclear charge as well as higher number of protons compared to electrons in the cations.
- Across the group, the the atomic and cationic sizes increases simply because more shells are added gradually.

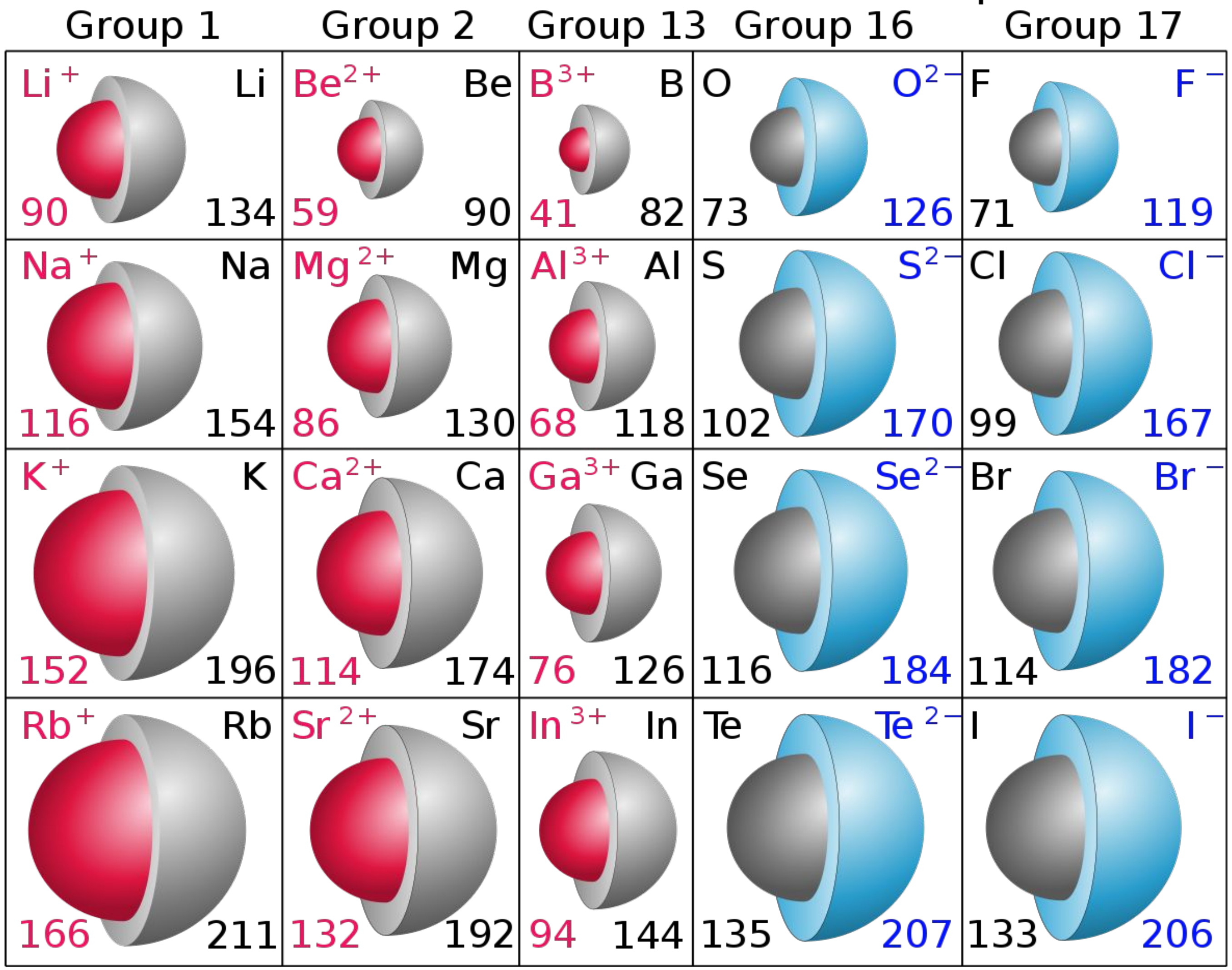
Atomic and ionic radius

- For nonmetals (right hand side of the periodic table, Group V, VI, VIIA), they accept electron to become -ve anions, and the size of their anion always increases as in the outermost shell interelectronic repulsion increases.
- Moreover, in anion the number of proton is lower than the number of electron as compared to neutral atom, as a result nuclear attraction become less effective.
- Along the period, the atomic and anionic sizes decreases as a result of increasing effective nuclear charge as well as decreasing charge of the stable anions.
- Across the group, the the atomic and anionic sizes increases simply because more shells are added gradually.

Periodic trends : Atomic radius



Sizes of atoms and their ions in pm



Ionization energy

The quantity of energy required to remove an electron from an atom is called as the ionization energy.

Ionization energy is usually expressed in terms of electron volt (eV) per atom or kJ/mole.

1 eV/atom = 96.48 kJ/mol

Low IE: Easy to remove an electron from the atom

High IE: Hard to remove an electron from the atom

Factors affecting the ionization energy

❖ **Effective nuclear charge**

- Higher the effective nuclear charge, higher the force of attraction between the nucleus and the electron and hence higher the ionization energy

❖ **Size of the atom**

- With the increase in the size of the atom, the electrons remain farther from the nucleus. As a result, the force of attraction between the nucleus and the outermost electron decreases and the ionization energy

Trend in Ionization energy

What happens down a group?

The ionization energy decreases down the group.

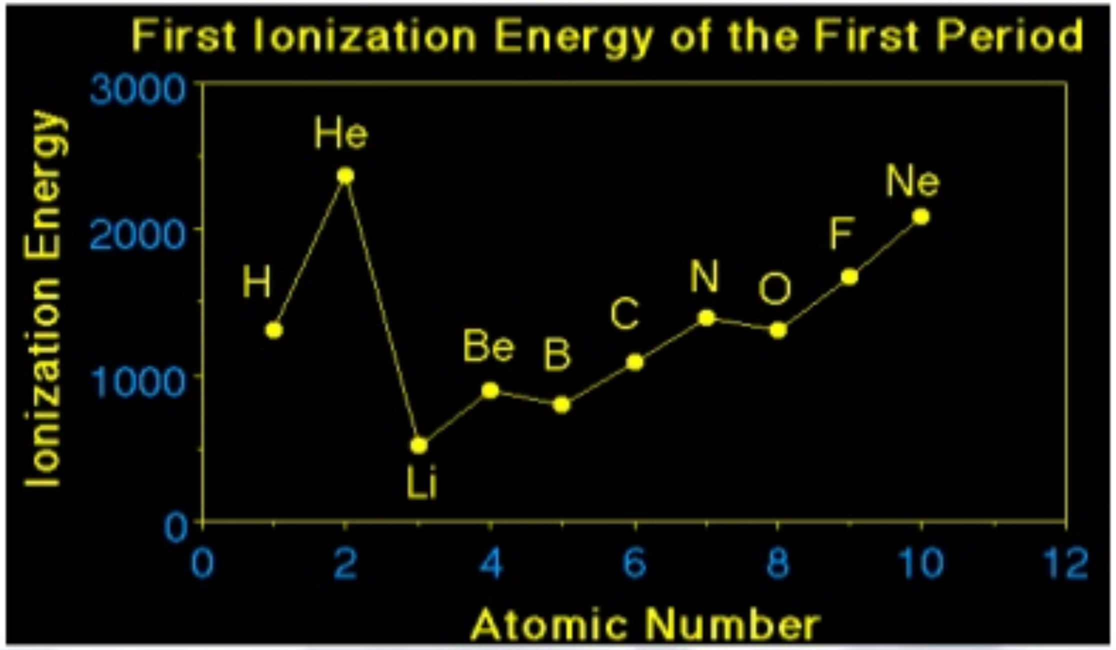
As the size of atom increases down the group, the attraction becomes weaker between the outer shell electrons and the nucleus. Hence less energy is required to remove an electron from the outermost shell.

What happens across a period?

The ionization energy increases along a period.

Across a period, as the size of atom decreases from left to right, the force of attraction between the nucleus and electrons increases. Hence higher energy is required to remove the electron from the outermost shell.

- As the period begins it does not take a lot of energy to remove an electron from Li but as you go across the period it takes more and more energy to take an electron away



Electron Affinity

The amount of energy released when an electron is added to a neutral atom in gaseous state is called as its electron affinity.

$$X(g) + e^- \longrightarrow X^-(g)$$

Factors affecting the electron affinity

❖ Effective nuclear charge

- Higher the effective nuclear charge of the atom, higher the force of attraction between the nucleus and the additional electron and hence higher the electron affinity

❖ Size of the atom

- Smaller the size of the atom, smaller will be the distance between the nucleus and the additional electron. As a result, the force of attraction between the nucleus and the outermost electron increases and the electron affinity increases with the smaller size of the atom.

❖ Electronic configuration

Atoms having stable electronic configuration (half-filled or full-filled outer orbitals) do not show much tendency for an extra electron. Hence they have either zero or very low electron affinity.

Trend in Electron Affinity

What happens down a group?

The electron affinity decreases down the group.
As the size of atom increases down the group, the attraction becomes weaker between the nucleus of atom and the additional electron.
Hence the atom possess less electron affinity.

What happens across a period?
The electron affinity increases on moving from left to right along a period.

Across a period, as the size of atom decreases from left to right, the force of attraction between the nucleus and electrons increases.
Hence the electron affinity increases along the period from left to right.

Electronegativity

The ability of an atom to attract the shared electrons towards itself is called as its electronegativity.

Note: Electronegativity is not a property of an atom alone, but rather a property of an atom in a molecule

- The term "electronegativity" was introduced by Jöns Jacob Berzelius in 1811.
- An accurate scale of electronegativity was not developed until 1932, when Linus Pauling proposed an electronegativity scale
- Electronegativity cannot be directly measured and must be calculated from other atomic or molecular properties.

Pauling electronegativity:

Let us consider the formation of A-B from A_2 and B_2

$$A\text{-}A + B\text{-}B \longrightarrow 2\ A\text{-}B$$

The molecular orbital for AB is:

$$\phi_{AB} = \psi_A + c\,(\psi_B)$$

If c > 1, then the molecular orbital is concentrated on atom B, which will acquire a partial negative charge.

$$\overset{\delta+}{A} - \overset{\delta-}{B}$$

The difference in electronegativity between atoms A and B is given by

$$|\chi_A - \chi_B| = (eV)^{-1/2}\,[E_d\,(AB) - (E_d\,(AA) + E_d\,(BB))/2]^{1/2}$$

where E_d represents the bond dissociation energy in eV

Mulliken electronegativity:

Robert S. Mulliken proposed that the arithmetic mean of the first ionization energy (E_i) and the electron affinity (E_{ea}) should be a measure of the tendency of an atom to attract electrons.

$$\chi = (E_i + E_{ea})/2 \text{ (in eV)}$$

Trend in Electronegativity

In general, electronegativity increases on passing from left to right along a period and decreases on descending a group.

Hence, fluorine is the most electronegative of the elements, whereas Francium is the least electronegative.