Republic of Iraq
Ministry of Higher Education & Scientific research
Al-Mustaqbal University
Science College
Biochemistry Department

Introduction in Chemistry

For

First Year Student

Lecture 6

By

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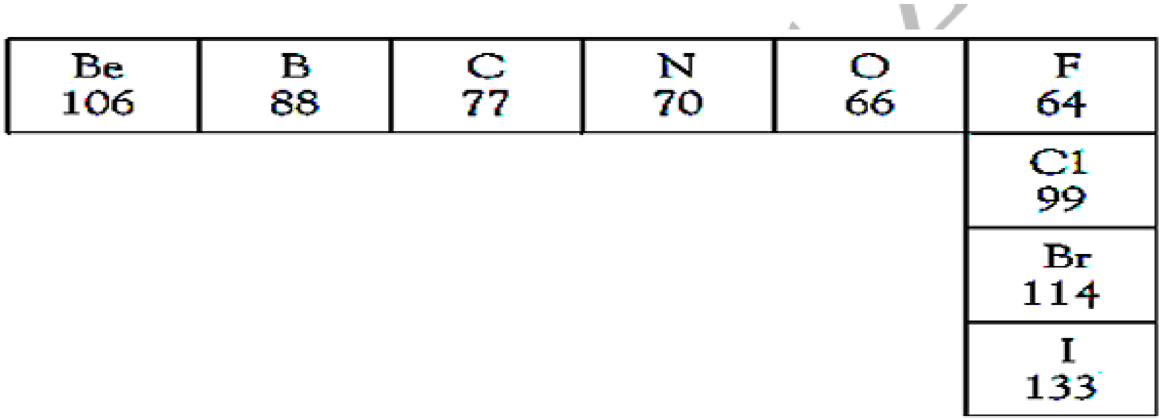
PERIODIC PROPERTIES

Atomic Radius : There are two common ways in which we can define atomic radius.

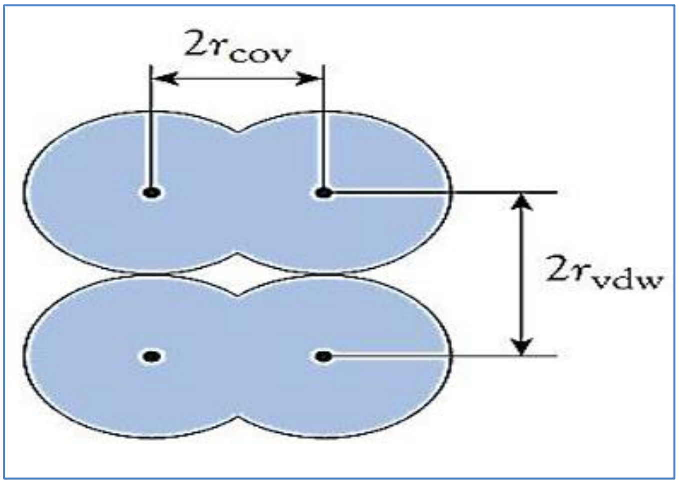
The covalent radius, r_{cov}, is defined as the half-distance between the nuclei of two atoms of the same element joined in a single covalent bond. The figure below represents the covalent radii (pm) of a typical group and short period.



Be 106	B 88	C 77	N 70	O 66	F 64
					Cl 99
					Br 114
					I 133

The van der Waals radius, r_{vdw}, is defined as the half-distance between the nuclei of two atoms of neighboring molecules.

The next figure shows comparison of the covalent radius, rcov, and the van der Waals radius, r_{vdw}.



<u>In a period, left to right</u>:

a- n (number of shells) remain constant.

b- Z increases (by one unit).

c- Z* increases (by 0.65 unit).

d- Atomic radius decreases.

In a group, top to bottom:

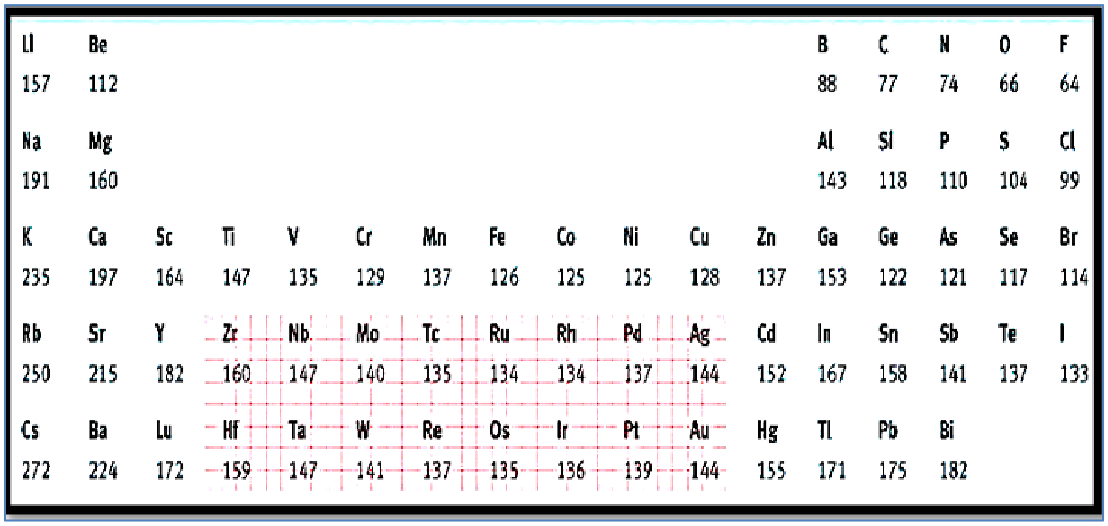
a- n increases.

b- Z increases.

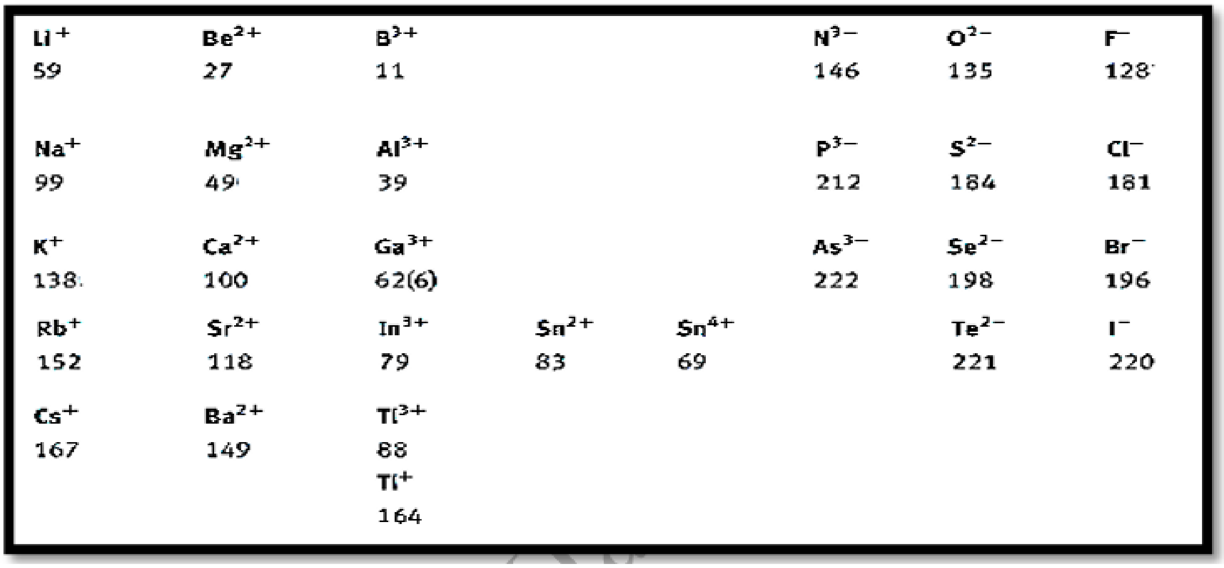
c- No dramatic increase in Z*, almost remains constant

d- -. Atomic radius increases.

The next two tables represent, respectively, the Atomic and Ionic Radii in (pm) unit, where pm = 10^{-12}m.



Li	Be											B	C	N	O	F
157	112											88	77	74	66	64
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	153	122	121	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	167	158	141	137	133
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	172	159	147	141	137	135	136	139	144	155	171	175	182		



Li^{+} 59	Be^{2+} 27	B^{3+} 11			N^{3-} 146	O^{2-} 135	F^{-} 128
Na^{+} 99	Mg^{2+} 49	Al^{3+} 39			P^{3-} 212	S^{2-} 184	Cl^{-} 181
K^{+} 138	Ca^{2+} 100	Ga^{3+} 62(6)			As^{3-} 222	Se^{2-} 198	Br^{-} 196
Rb^{+} 152	Sr^{2+} 118	In^{3+} 79	Sn^{2+} 83	Sn^{4+} 69		Te^{2-} 221	I^{-} 220
Cs^{+} 167	Ba^{2+} 149	Tl^{3+} 88 Tl^{+} 164					

To explain this change in atomic size through a period, we take the example of the lithium atom, which has the following atomic arrangement:

3Li : $1S^{2}\ 2S^{1}$

We notice that the outer shell electron($2S^{1}$) is only blocked by the inner shell or core electrons($1S^{2}$)from the total attraction of the three protons present in the nucleus of the lithium atom, where the force of attraction of the positive protons present in the nucleus to the negative electron is called **effective nuclear charge** (Z *).

Let's take another example, which is the beryllium atom, which has the following electronic configuration:

4Be : $1S^{2}\ 2S^{2}$

We notice that the last electron in this atom is not only prevented by the inner electrons (the two electrons of the 1s2 shell) from attracting the effective charge of the nucleus, but it is also prevented by the electron present with it in the same shell, but the shielding caused by the electron present with it is much less than the shielding caused by the electrons present in the inner shells.

Therefore, the last electron in beryllium will feel a higher attraction force from the four protons in the nucleus, compared to the attraction force of the three protons of lithium, so the atomic radius of beryllium is smaller than the atomic radius of lithium.

Note: In one period from left to right, the shielding decreases, the effective charge increases, and the atomic size or radius also decreases.

Rules Slater's

$$Z^* = Z - S$$

Z^*: effective nuclear charge

Z :Atomic number

S: shielding constant

1. Write the electron configuration of the atom in the following form:

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) (5d)

2. All electrons in orbitals of greater principal quantum number (at n+1) contribute zero.

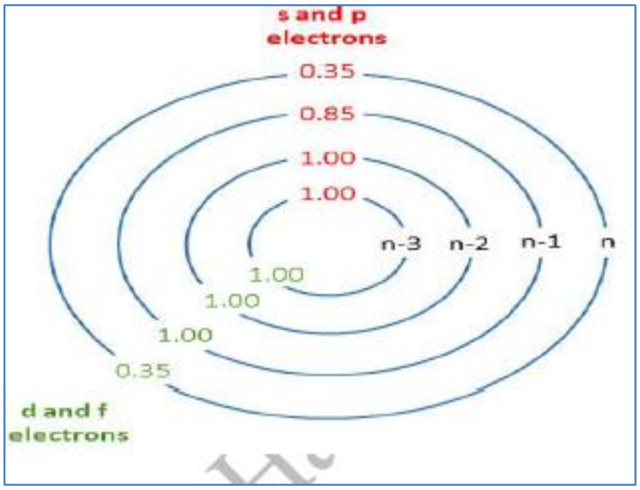
3.For **ns** or **np** valence electrons:

a. Electrons in the ***same*** **ns, np** group (same principal quantum number) contributes **(0.35)**.

b. Electrons in the (n-1) principal group contribute (0.85).

c. Electrons in the (n-2) or lower groups contribute (1.00).

4- For **nd** and **nf** valence electrons:



Example: Calculate the effective nuclear charge (Z*) of the following:

a- 2p electron in the $_8$O atom.

Ans. $_8O : (1S^2)\ (2S^2\ 2P^4) = (1S)^2\ (2S\ 2P)^6$

$S = (2 \times 0.85) + (5 \times 0.35) = 3.45$

Z* = Z – S = 8 - 3.45= **4.55**

b- **3d electron in the 28Ni atom**.

Ans. $_{28}Ni = (1S^2)\ (2S^2\ 2p^6)\ (3S^2\ 3p^6)\ (4S^2)\ (3d^8)$

$= (1S)^2\ (2S2p)^8\ (3S\ 3p)^8\ (3d)^8\ (4S^2)$

S $= [18 \times (1)] + [7 \times (0.35)] = 20.45$

$Z^* = Z - S = 28 - 20.45 = 7.55$

c- 4s electron in the $_{28}$Ni atom.

Ans. $_{28}Ni = (1S^2)\ (2S^2\ 2P^6)\ (3S^2\ 3P^6)\ (4S^2)\ (3d^8)$

$= (1S2S\ 2P)^{10}\ (3S\ 3P3d)^{16}\ (4S)^2$

$S = [10 \times (1)] + [16 \times (0.85)] + [1 \times (0.35)] = 23.95$

$Z^* = Z – S = 28 – 23.95 = 4.05$

d- 4f electron in the $_{73}$Ta atom.

Ans. $_{73}Ta = [Xe]_{54}\ 4f^{14}\ 6S^2\ 5d^3$

$= [Xe]_{54}\ 4f^{14}\ (6S)^2\ (5d)^3$

$S = [54 * (1)] + [13 * (0.35)] = 58.55$

$Z^* = Z – S = 73 – 58.55 = 14.45$

e- The last electron in $_{29}$Cu atom.

Ans. $_{29}Cu = (1S^2)\ (2S^2\ 2P^6)\ (3S^2\ 3P6)\ (4S^1)\ (3d^{10})$

$= (1S2S\ 2P)^{10}\ (3S\ 3P3d)^{18}\ (4S)^1$

$S = [10 \times (1)] + [18 \times (0.85)] + [0 \times (0.35)] = 25.30$

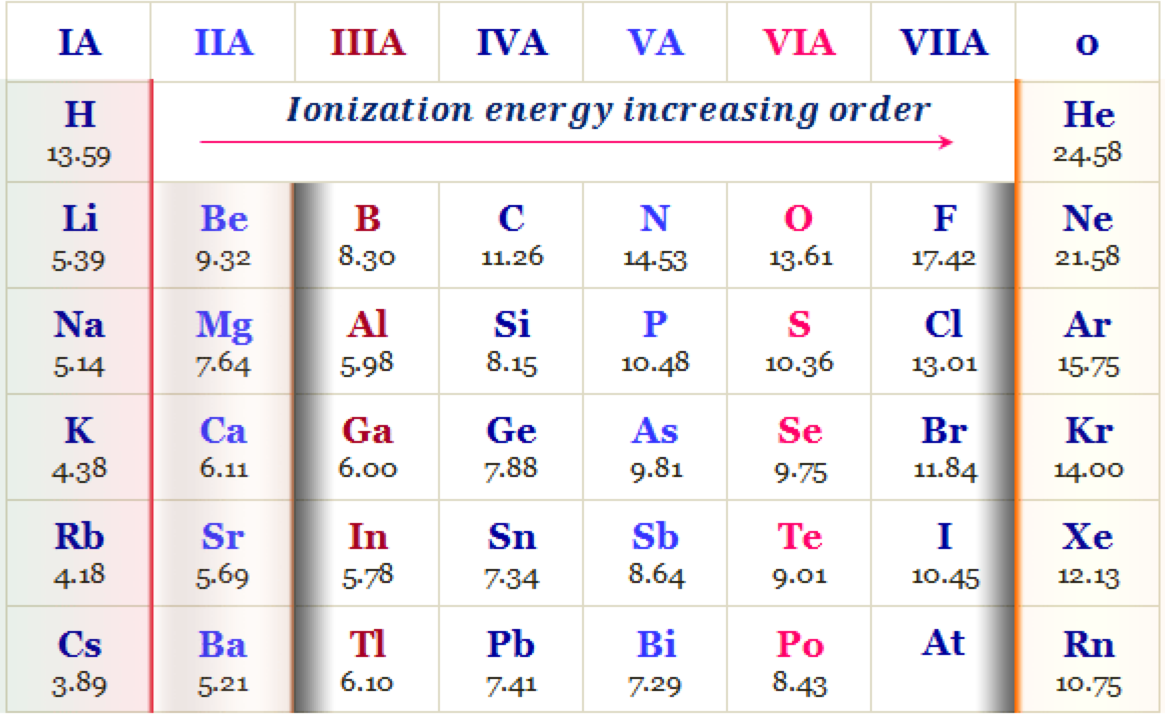
$Z^* = Z – S = 29 – 25.30 = 3.70$

It is clear from the above that in one period from left to right, the effective charge of the nucleus increases and the shielding and size decrease.

Ionization Energy (IE):- also known as the **ionization potential**, Is the energy required to remove an electron from a gaseous atom to form a gaseous cation. The losing of an electron is an **Endothermic** process (require energy).

$$X(g) + \text{energy} \rightarrow X^{+}(g) + e^{-}$$

- It became clear from studying the effective charge of the nucleus that the electrons of the outer shell are linked by the force of attraction of the protons of the positive nucleus of the atom, and therefore to overcome this attractive energy the electron must be supplied with energy.
- The first ionization energy always requires less energy than the second ionization energy. The reason is that the second valence electron suffers from a higher attractive force(Z*) than the first valence electron.
- Ionization energy increases in the period (from left to right) due to the increase in the effective charge of the nucleus (Z*) and decreases in the group (from top to bottom) as shown in the table below.



IA	IIA	IIIA	IVA	VA	VIA	VIIA	o
H 13.59	*Ionization energy increasing order* →						**He** 24.58
Li 5.39	**Be** 9.32	**B** 8.30	**C** 11.26	**N** 14.53	**O** 13.61	**F** 17.42	**Ne** 21.58
Na 5.14	**Mg** 7.64	**Al** 5.98	**Si** 8.15	**P** 10.48	**S** 10.36	**Cl** 13.01	**Ar** 15.75
K 4.38	**Ca** 6.11	**Ga** 6.00	**Ge** 7.88	**As** 9.81	**Se** 9.75	**Br** 11.84	**Kr** 14.00
Rb 4.18	**Sr** 5.69	**In** 5.78	**Sn** 7.34	**Sb** 8.64	**Te** 9.01	**I** 10.45	**Xe** 12.13
Cs 3.89	**Ba** 5.21	**Tl** 6.10	**Pb** 7.41	**Bi** 7.29	**Po** 8.43	**At**	**Rn** 10.75

It is noted that the ionization energy of oxygen is less than that of nitrogen, despite the increase in ionization energy when moving in one period from left to right. The reason for this is that the $(2P^{3})$ orbital in nitrogen has three electrons distributed singly (semi-saturated orbitals are more stable). However, in the case of oxygen ($2P^4$), the presence of a fourth electron will be added to the semi-saturated orbital, which reduces stability and reduces the energy required to extract the electron.

- ✓ It is noted that the ionization energy and the effective nucleus charge (Z*) increase in the period (from left to right), which means that there is a direct relationship between them, and at the same time there is an inverse relationship between the square of the period number (n) and the ionization energy, which explains the decrease in ionization energy in the same group when descending from top to bottom. The relationship below shows the relationship between ionization energy, the effective charge of the nucleus and the period number (principal quantum number).

$$IE \propto \frac{(Z^*)^2}{n^2}$$

$$I.E = 13.6\ e.v * \frac{(Z^*)^2}{n^2}$$

Z* = Effective nuclear charge.

n = principle quantum number.

13.6 e.v = The ionization energy of the H atom.

This value (-13.6 ev)represents the energy of the electron in the hydrogen atom, and therefore, to remove the electron from the hydrogen atom, it must be exposed to a potential difference (energy) of 13.6 ev.

Ex: Calculate the first ionization energy or (potential) of $_3$Li

Ans: First we must calculate Effective nuclear charge (Z*)

$_3$Li: $(1S)^2\ (2S)^1$

S = [2×(0.85)] + [0× (0.35)] = 1.7

Z* = Z – S = 3 – 1.7 = 1.3

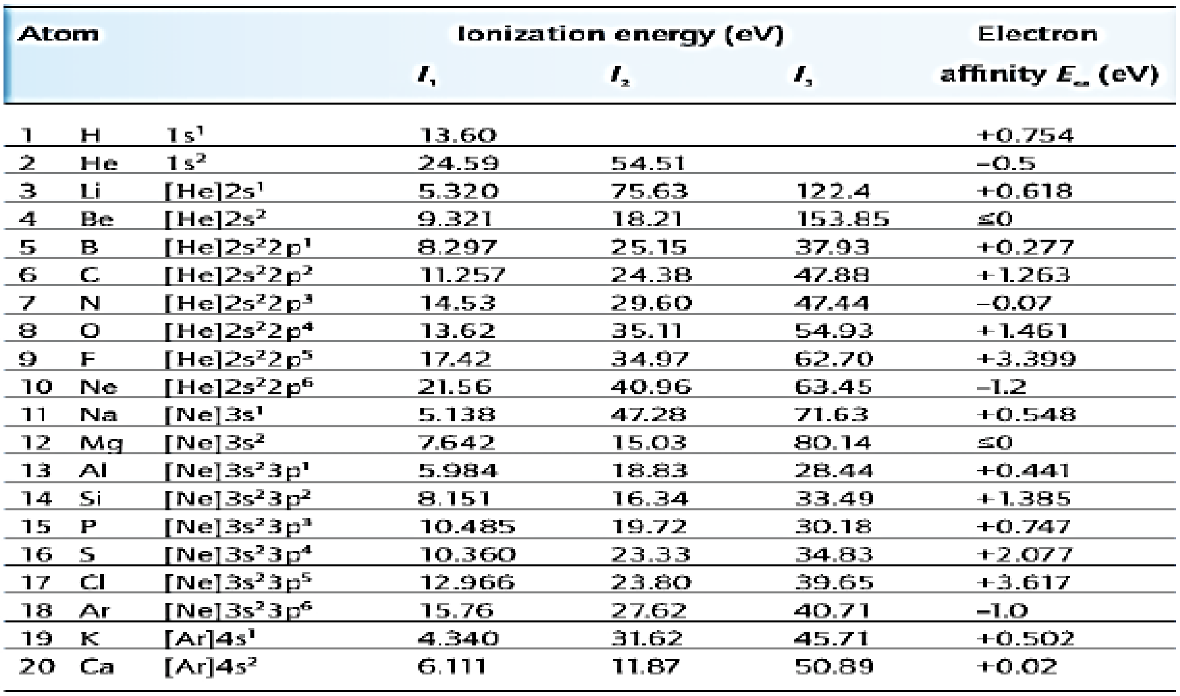
So I.E = 13.6 e.v $*[(Z^*)^2 / n^2]$

= 13.6 e.v $* [(1.3)^2/ (2)^2]$

= 13.6 e.v * [0.4225] = 5.746 e.v

So, **I.E** of **$_3$Li** in KJ/ mol = [5.746] ***** [96.485]

= 554.4 KJ/ mol



Atom			Ionization energy (eV)			Electron
			I_1	I_2	I_3	affinity E_{ea} (eV)
1	H	$1s^1$	13.60			+0.754
2	He	$1s^2$	24.59	54.51		−0.5
3	Li	$[He]2s^1$	5.320	75.63	122.4	+0.618
4	Be	$[He]2s^2$	9.321	18.21	153.85	≤0
5	B	$[He]2s^22p^1$	8.297	25.15	37.93	+0.277
6	C	$[He]2s^22p^2$	11.257	24.38	47.88	+1.263
7	N	$[He]2s^22p^3$	14.53	29.60	47.44	−0.07
8	O	$[He]2s^22p^4$	13.62	35.11	54.93	+1.461
9	F	$[He]2s^22p^5$	17.42	34.97	62.70	+3.399
10	Ne	$[He]2s^22p^6$	21.56	40.96	63.45	−1.2
11	Na	$[Ne]3s^1$	5.138	47.28	71.63	+0.548
12	Mg	$[Ne]3s^2$	7.642	15.03	80.14	≤0
13	Al	$[Ne]3s^23p^1$	5.984	18.83	28.44	+0.441
14	Si	$[Ne]3s^23p^2$	8.151	16.34	33.49	+1.385
15	P	$[Ne]3s^23p^3$	10.485	19.72	30.18	+0.747
16	S	$[Ne]3s^23p^4$	10.360	23.33	34.83	+2.077
17	Cl	$[Ne]3s^23p^5$	12.966	23.80	39.65	+3.617
18	Ar	$[Ne]3s^23p^6$	15.76	27.62	40.71	−1.0
19	K	$[Ar]4s^1$	4.340	31.62	45.71	+0.502
20	Ca	$[Ar]4s^2$	6.111	11.87	50.89	+0.02

Electron Affinity (EA): is defined as the amount of energy released when an electron is attached to a neutral atom in the gaseous state to form a negative ion.. The gaining of an electron is an exothermic process (releasing energy).

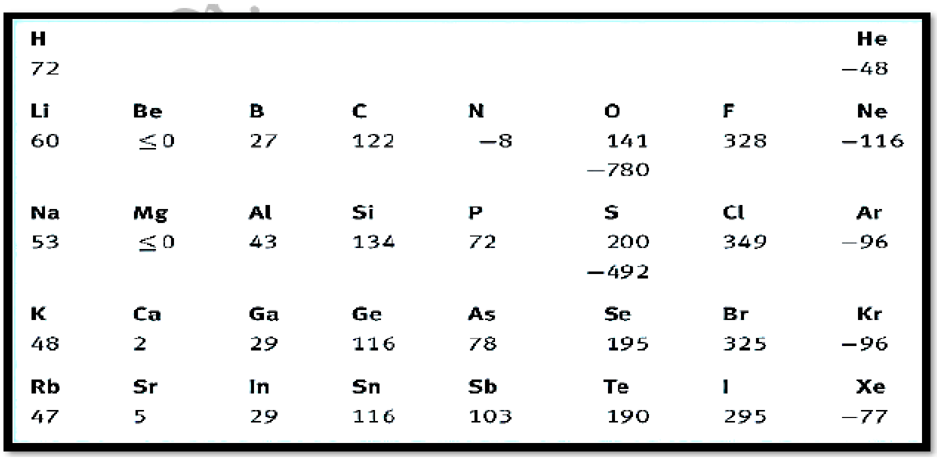
$$X(g) + e^{-} \rightarrow X^{-}(g) + Energy$$

The energy released when an electron is added to a neutral atom is a measure of the strength of the bond between this electron and the atom. The greater the energy released, the more strongly the added electron is bound. Since the atomic radius decreases in the period, this means that the added electron will be closer to the nucleus (i.e. will be more strongly bound) as we move from left to right in the period. Therefore, the electron affinity increases in the period from left to right and decreases in the group from top to bottom.

Note1 :that the electron affinity of metals is low and that of non-metals is high.

Note2: Halogens have a high electron affinity, due to their strong desire to gain an electron to fill their outer shell (i.e. until it is filled with eight electrons) and become more stable.

The following table shows the electron affinity values of the elements represented in kj/mole.



H 72							**He** −48
Li 60	**Be** ≤0	**B** 27	**C** 122	**N** −8	**O** 141 −780	**F** 328	**Ne** −116
Na 53	**Mg** ≤0	**Al** 43	**Si** 134	**P** 72	**S** 200 −492	**Cl** 349	**Ar** −96
K 48	**Ca** 2	**Ga** 29	**Ge** 116	**As** 78	**Se** 195	**Br** 325	**Kr** −96
Rb 47	**Sr** 5	**In** 29	**Sn** 116	**Sb** 103	**Te** 190	**I** 295	**Xe** −77

<u>Electronegativity</u>;- Pauling defined electronegativity as **the power of an atom in a molecule to attract a shared pair of electrons (or electron density) to itself**.

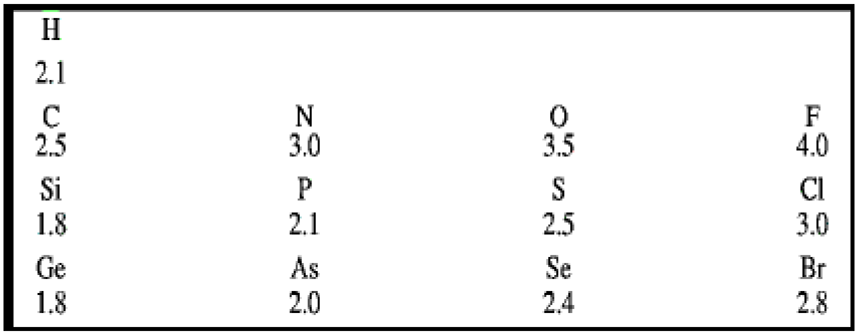
*Other definition

<u>Electronegativity:</u> is a measure of an atom's ability to attract electrons from a neighboring atom to which it is bonded.

Note1: All periodic properties are specific to atoms except for negativity, which is specific to molecules.

Note2: The higher the effective charge of the nucleus of an atom within a molecule, the more this atom shows a desire to attract electrons towards it. Therefore, the electronegativity increases in one period (from left to right) and decreases in the group (from top to bottom).

The table below shows the electronegativity values of a group of representative elements.



H 2.1			
C 2.5	N 3.0	O 3.5	F 4.0
Si 1.8	P 2.1	S 2.5	Cl 3.0
Ge 1.8	As 2.0	Se 2.4	Br 2.8