Electronegativity (EN)

What is Electronegativity ?

When two different atoms in a molecule are bonded together by a covalent bond, the electron pair forming the covalent bond is not shared equally by both the atoms. Rather, the electron pair lies nearer to one atom than the other. *The relative tendency (or ability or power) of a bonded atom in a molecule to attract the shared electron pair towards itself is termed as its electronegativity.*

This definition was given by Pauling in 1932. Electronegativity is an inherently fundamental property of the atom and is fundamentally different from electron affinity, since electron affinity represents the tendency of an *isolated gaseous atom* to attract the electrons while electronegativity represents the tendency of a bonded atom (*i.e.* of an atom in a molecule) to attract the shared electron pair.

Scales of Electronegativity : Measurement of Electronegativity.

A number of scales have been devised to measure the electronegativity of the atoms. These scales are arbitrary and are based on various types of experimental data like bond energy, dipole moment, ionisation potential and electron affinity. More commonly used scales are described below :

1. Pauling's Scale (1932). This scale is based on an empirical relation between the energy of a bond (called *bond energy*) and the electronegativities of the bonded atoms. Let us consider a A–B bond between two dissimilar atoms, A and B of a molecule AB. Let the bond energies of A–A, B–B and A–B bonds be represented as E_{A-A}, E_{B-B} and E_{A-B} respectively.

What is electronegativity

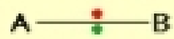
Definition

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to caesium and francium which are the least electronegative at 0.7.

What happens if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. Each atom may be forming other bonds as well as the one shown - but these are irrelevant to the argument.



If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found *on average* half way between the two atoms. To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules.

Note: It's important to realise that this is an *average* picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital.

This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.

Factors Affecting the Magnitude of Electronegativity

Following are the important factors on which the magnitude of electronegativity depends

1. Size of the atom. The smaller the size of an atom, greater is its tendency to attract towards itself the shared pair electrons.

Thus the smaller atoms have greater electronegativity values than the larger atoms. For example :

(*a*) Electronegativity values of the elements of group IA decrease from H(Z = 1) to Cs(Z = 55), since the atomic (covalent) radii of these elements increase in the same order as shown below :

Elements of group IA	Atomic (covalent) radius (Å)	Electronegativity
H (1)	0.32	2.1
Li(3)	1.23	1.0
Na (11)	1.54	0.9
K (19)	2.03	0.8
Rb (37)	2.16	0.8
Cs (55)	2.35	0.7
	Increasing ↓	*Decreasing* ↓

(*b*) Electronegativity values of the elements of 2*nd* period increase from Li (Z = 3) to F(Z = 9), since the atomic (covalent) radii of these elements decrease in the same order as shown below :

Elements of 2nd period	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*
Atomic (covalent) radius (Å)	*1.23*	*0.90*	*0.82*	*0.77*	*0.75*	*0.73*	*0.72*
	Decreasing →						
Electronegativity	*1.0*	*1.5*	*2.0*	*2.5*	*3.0*	*3.5*	*4.0*
	Increasing →						

2. Number of inner shells. *The atom with greater number of inner shells (i.e. the shells between the nucleus and the outer-most shell) has less value of electronegativity than the atom with smaller number of inner shells.* For example the electronegativity values of halogens decrease from F(Z = 9) to At(Z = 85), since the number of inner shells increases in the same order as shown below :

Table 4.12 makes it evident that, in general, the electronegativity values of M, M^+ and M^{2+} species are in the order :

$$M^{2+} > M^+ > M,$$

while the size of these species is in the reverse order as shown below :

$$M^{2+} < M^+ < M$$

An anion attracts the electron pair less readily than its parent atom. This is also due to the fact that an anion is larger in size than its parent atom ($X^- > X$). *Thus an anion, X^- has less electronegativity than its parent atom, X, i.e.*

Order of electronegativity : $X^- < X$

Order of size : $X^- > X$

The above point is clear from the fact that F^- ion has less electronegativity value than F atom ($F^- = 0.8$. $F = 4.0$).

4. Number and nature of atoms to which the atom is bonded. We have seen that, since electronegativity of an atom is not the property of this atom in its isolated state, it depends on the number and nature of the atoms to which the atom is bonded. For this reason the electronegativity value of an atom is not constant. For example electronegativity value of P atom in PCl_3 molecule is different from that in PF_5 molecule in which the number and nature of the atoms both to which P atom is bonded change.

5. Ionisation energy and electron affinity. The numerical value of electronegativity of the atom of an element also depends both on the magnitude of ionisation energy and electron affinity. Higher ionisation energy of an atom means that it is difficult to remove the most loosely bonded electron from the atom which leads us to expect that the electron affinity of that atom will also be greater. *Thus the atoms of the elements which have higher values of ionisation energy and electron affinity also have higher values of electronegativity.* For example, the elements of group VII A (halogens) which have the highest ionisation energies and electron affinities also have the highest values of electronegativity. Similarly, the elements of group IA (alkali metals) which have the lowest ionisation energies and electron affinities have the lowest values of electronegativity.

6. Type of hybridisation. The magnitude of electronegativity of an atom also depends on the type of hybridisation which the atom undergoes in the formation of different bonds in the molecule. *The magnitude of electronegativity increases as the s-character in hybrid orbitals increases.*

Example : The electronegativity of carbon atom in methane (sp^3 hybridisation with 25% *s*-character), ethylene (sp^2 hybridisation with 33% *s*-character) and acetylene (*sp* hybridisation with 50% *s*-character) is in the increasing order as shown below :

Hydrocarbon	:	*Methane* (CH_4)	*Ethylene* ($H_2C = CH_2$)	*Acetylene* ($CH \equiv CH$)
Type of hybridisation	:	sp^3	sp^2	sp
Amount of s-character in hybrid orbitals	:	*25%*	*33%*	*50%*
Order of electronegativity of carbon atom	:	———	*Increasing* ⟶	

Variation of Electronegativity in a Period and a Group of Representative Elements : *Periodic Trends of Electronegativity*

(*a*) **In a period.** *In going from left to right in a period of s- and p-block elements, the electronegativity values increase.* This increase can be explained on the basis of any of the following facts.

(*i*) On moving from left to right in a period, there is a decrease in the size of the atoms. Smaller atoms have greater tendency to attract the electrons towards themselves *i.e. smaller atoms have higher electronegativity values.*

(*ii*) On moving from left to right in a period there is an increase of ionisation energy and electron affinity of the elements. The atoms of the elements which have higher value of ionisation energies and electron affinities also have higher electronegativities.

(*b*) **In a group.** *In going down a group of s- and p-block elements, the electronegativity values decrease.* This decrease can also be explained on the basis of any of the following facts.

(*i*) As we move down a group, there is an increase in the size of the atoms. With the increase in size of the atoms, their electronegativity values decrease.

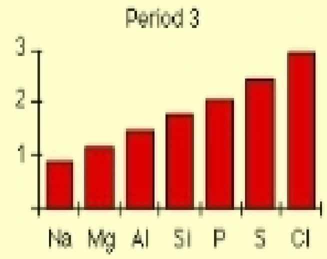
(*ii*) Ionisation energy and electron affinity on which electronegativity depends decrease as the group is descended. With the decrease of these quantities the electronegativity values also decrease.

The heavier elements of group III A (*i.e.* Ga, In and Tl) show *reverse trend* due to the intervening transition series.

The variation of electronegativity values discussed above reveals that the *halogens* (VII A group elements) which lie on the extreme right of the periodic table are the *most electronegative* (*i.e. least electropositive*) *elements and the alkali metals* (IA group elements) which lie on the extreme left of the periodic table are the *least electronegative* (*i.e. most electropositive*) *elements*. Thus we see that the *most electronegative element is flourine* which occurs at the top right hand corner and the *least electronegative* element is *cesium* which occurs at the bottom left hand corner of the periodic table. Being the most electronegative, F does not show any basic character, *i.e.*, it has no tendency to form positive ions in any of its known compounds. On the other hand, there is, however, evidence to show that Cl, Br and I have a tendency to form positive ions.

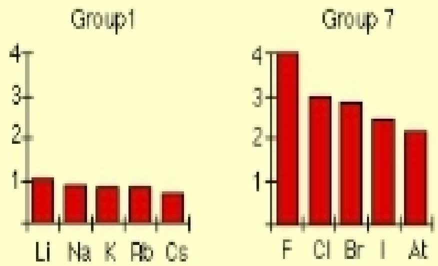
Trends in electronegativity across a period

As you go across a period the electronegativity increases. The chart shows electronegativities from sodium to chlorine - you have to ignore argon. It doesn't have an electronegativity, because it doesn't form bonds.



Trends in electronegativity down a group

As you go down a group, electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.) The chart shows the patterns of electronegativity in Groups 1 and 7.



Explaining the patterns in electronegativity

The attraction that a bonding pair of electrons feels for a particular nucleus depends on:

- the number of protons in the nucleus;
- the distance from the nucleus;
- the amount of screening by inner electrons.

Explaining the diagonal relationship with regard to electronegativity

Electronegativity increases across the Periodic Table. So, for example, the electronegativities of beryllium and boron are:

Be	1.5
B	2.0

Electronegativity falls as you go down the Periodic Table. So, for example, the electronegativities of boron and aluminium are:

B	2.0
Al	1.5

So, comparing Be and Al, you find the values are (by chance) exactly the same.

The increase from Group 2 to Group 3 is offset by the fall as you go down Group 3 from boron to aluminium.

Something similar happens from lithium (1.0) to magnesium (1.2), and from boron (2.0) to silicon (1.8).

In these cases, the electronegativities aren't *exactly* the same, but are very close.

Similar electronegativities between the members of these diagonal pairs means that they are likely to form similar types of bonds, and that will affect their chemistry. You may well come across examples of this later on in your course.