# Electronegativity.

**The tendency of an atom in a compound to attract a pair of bonded electrons towards itself is known as electronegativity of the atom**. It is important to note that electron affinity and electronegativity both measure the electrons attracting power but the former refers to an isolated gaseous atom while the latter to an atom in a compound. Thus electron affinity is attraction for a single electron while electronegativity is for a pair of bonded electrons. Further electron affinity is energy while electronegativity is a tendency.

(1) **Factors affecting the value of electronegativity**

(i) The size of the atom.

(ii) Electronic configuration. Small atoms attract electrons more than the larger one and are therefore more electronegative. Secondly, atoms with nearly filled shell of electrons, will tend to have higher electronegativity than those sparsely occupied ones.

(2) **Variation of electronegativity in the periodic table**

(i) In a period, electronegativity increases from left to right. This is due to decrease in size and increase in nuclear charge. Thus the alkali metals possess the lowest value, while the halogens have the highest. Inert gases have zero electronegativity.

(ii) In a group, electronegativity decreases from top to bottom. This is due to increase in atomic size.

If an element exhibits various oxidation state, the atom in the higher oxidation state will be more negative due to greater attraction for the electron, e.g., Sn II (1.30) and Sn IV (1.90).

(3) Electronegativity may be expressed on the following three scales

(i) **Mulliken'sscale:**Mulliken regarded electronegativity as the average value of ionization potential and electron affinity of an atom.

$$\text{Electronegativity} = \frac{\text{Ionization potential} + \text{Electron affinity}}{2}$$

(ii) **Allred-Rochowscale:** Allred and Rochow defined electronegativity as the electrostatic force exerted by the nucleus on the valence electrons. Thus $\chi = \frac{0.359\ Z}{r^2} + 0.744$ where Z is the effective nuclear charge and r is the covalent radius of the atom in Å.

(iii) **Pauling scale:** Pauling scale of electronegativity is the most widely used. It is based on excess bond energies. He determined electronegativity difference between the two atoms and then by assigning arbitrary values to few elements (e.g. 4.00 to fluorine, 2.5 to carbon and 2.1 to hydrogen), he calculated the electronegativity of the other elements. $\chi_A - \chi_B = 0.208\sqrt{\Delta E}$
Where $\chi_A$ and $\chi_B$ are electronegativities of the atoms A and B respectively, the factor 0.208 arises from the conversion of kcal to electron volt (1 eV = 23.0 kcal/mole), while $\Delta E =$ Actual bond energy $-\sqrt{(E_{A-A} \times E_{B-B})}$
Pauling and Mulliken values of electronegativity's are related as below $\chi$ (Pauling) = $0.34\chi$ (Mulliken) – 0.2

(4)**Importance of electronegativity:** The following predictions can be made from value of electronegativity,

(i) Nature of the bond between two atoms can be predicted from the electronegativity difference of the two atoms.

(a) The difference $X_A - X_B = 0,$ i.e., $X_A = X_B$ the bond is purely covalent.

(b) The difference $X_A - X_B$ is small, i.e., $X_A > X_B$, the bond is polar covalent.

(c) The difference $X_A - X_B$ is 1.7, the bond is 50% covalent and 50% ionic.

(d) The difference $X_A - X_B$ is very high, the bond is more ionic and less covalent. The molecule will be represented in such case as $BA\ (B^+A^-)$.
Percentage ionic character may be calculated as,
Percentage of ionic character $= 16|X_A - X_B| + 3.5(X_A - X_B)^2$

Where $X_A$ and $X_B$ represents electronegativity of bonded atoms A and B.
This relation was given by A.L. Allerd (1961).

(ii) Greater the value of difference $(X_A - X_B)$ more stable will be the bond.

| | $H-F$ | $H-Cl$ | $H-Br$ | $H-I$ |
|---|---|---|---|---|
| $(X_A - X_B)$ | 1.9 | 0.9 | 0.7 | 0.4 |

Stability decreases →

Stability of compounds in which $X_A - X_B$ is very small are unstable in nature,
$SiH_4(o.3), NCl_3(0.0)$, $PH_3(0)$, $AsH_3(0.1)$ are unstable.

(iii) $(X_O - X_A)$ Difference predicts the nature of the oxides formed by the element A. $X_O$ is the electronegativity of oxygen.

$X_O - X_A$ is large, the oxide shows basic nature, (e.g., $Na_2O$ ).

$X_O - X_A$ is small, the oxide shows acidic nature, (e.g., $SO_2$).

(iv) Ionic compounds having percentage ionic character less than 20% were found coloured, e.g.,

| AgCl | AgBr | AgI | $Ag_2S$ |
|---|---|---|---|
| 22% | 18% | 11% | 8% |
| White | Light yellow | Dark yellow | Black |

Lesser the percentage ionic character, darker will be the colour.