Electronegativity

Introduction:

The tendency of an atom to attract a shared pair of electrons (or electron density) towards itself is known as electronegativity.

OR

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 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 atom .These scales are arbitrary and are based on various types of experimental data like bond energy, dipole moment, ionization potential and electron affinity. More commonly used scales are described below

Pauling Scale:

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 by

E_{A-A}, E_{B-B} and E_{A-B} respectively.

It has been seen that the energy of A-B bond (E_{A-B}) is almost always great than the geometric mean of the energies of A-A (E_{A-A}) and B-B (E_{B-B}) bonds, i.e.

$$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$$

The difference between E_{A-B} and $\sqrt{E_{A-A} \times E_{B-B}}$ is called **ionic-resonance energy** of A-B bond and is denoted by Δ_{A-B}. It is thus given by

$$\boldsymbol{\Delta_{A-B}} = \mathbf{E_{A-B}} - \sqrt{\mathbf{E_{A-A} \times E_{B-B}}} \qquad \text{.... i}$$

$\boldsymbol{\Delta_{A-B}}$ values do not possess additive property, i.e. if we consider three covalent bonds viz. A-B, B-C and C-A, then the sum of $\boldsymbol{\Delta_{A-B}}$ and $\boldsymbol{\Delta_{B-C}}$ is not equal to $\boldsymbol{\Delta_{C-A}}$ which means that :

$$\boldsymbol{\Delta_{A-B}} + \boldsymbol{\Delta_{B-C}} \neq \boldsymbol{\Delta_{C-A}} \qquad \text{....ii}$$

The relation (i) is true when the electronegativities of A, B and C are in order:

$$x_A > x_B > x_c.$$

The validity of relation (i) given above can be verified by calculating values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} for F-O, O-Si and F-Si covalent bond (electronegativities of F, °and Si are in the order: $x_F > x_o > x_s$) by using given bond energy values of F-O, O-Si, F-Si, F-F, 0-0 and Si-Si bonds

$E_{F-O} = 184.14$ KJ mole^{-1}; $E_{O-Si} = 372.46$ KJ mole^{-1}

$E_{F-si} = 535.58$ KJ mole^{-1}, $E_{F-F} = 154.84$ KJ mole^{-1}

$E_{o-o} = 138.10$ KJ mole^{-1} $E_{Si-Si} = 179.95$ KJ mole^{-1}

Thus by using relation (i), we can calculate the values of Δ_{F-O}' ~i and ~ for F-O, O-Si and F-Si bonds as shown below:

$\Delta_{F-O} = E_{F-O} - E_{F-F} \times E_{o-o}$

    $= 184.14 - 154.84 \times 138.10$

    $= 184.14 - 146.23 = 37.91$ kJ.mole^{-1}

$\Delta_{O-Si} = E_{O-Si} - E_{o-o} \times E_{Si-Si}$

     $= 372.46 - 138.10 \times 179.95$

     $= 372.46 - 157.64 = 214.82$ kJ.mole^{-1}

$\Delta_{F-Si} = E_{F-Si} - E_{F-F} \times E_{Si-Si}$

    $= 535.58 - 154.84 \times 179.95$

    $= 535.58 - 166.92 = 368.66$ kJ.mole^{-1}

With the help of the values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} as calculated above it be shown that

$$\Delta_{F-O} + \Delta_{O-Si} \neq \Delta_{F-Si}$$

$$37.91 + 214.82 \neq 368.66$$

$$252.73 \neq 368.66$$

We have already mentioned that the values of ionic-resonance energy i.e. (Δ_{A-B} values) do not show additive property. However it has been found that square roots of these values do show nearly the additive property, i.e. if we again consider the bonds viz. A-B, B-C and C-A, then the sum of $\sqrt{\Delta_{A-B}}$ and $\sqrt{\Delta_{B-C}}$ is nearly equal to $\sqrt{\Delta_{C-A}}$, i.e.

$$\sqrt{\Delta_{A-B}} + \sqrt{\Delta_{B-C}} \approx \sqrt{\Delta_{C-A}} \qquad \text{.....(iii)}$$

The validity of relation (iii) can be verified by the fact that for F-O, O-Si and F-Si bonds the sum of $\sqrt{\Delta_{F-O}}$ and $\sqrt{\Delta_{O-Si}}$ is almost equal $\sqrt{\Delta_{F-Si}}$ to as shown below:

$$\sqrt{\Delta_{F-O}} + \sqrt{\Delta_{O-Si}} \approx \sqrt{\Delta_{F-Si}}$$

$$37.91 + 214.82 \approx 368.66$$

$$6.15 + 14.65 \approx 19.20$$

$$20.80 \approx 19.20$$

The square root of ionic-resonance energy (i.e. $\sqrt{E_{A-B}}$) is a measure of the partial ionic character of an A-B covalent bond. With the increase of ionic character of A-B covalent bond, the magnitude of $\sqrt{E_{A-B}}$ also increases. The difference in electronegativity between the bonded atoms (A and B), $x_A - x_B$ ($x_A > x_B$) also increases with the increase of partial ionic character of A-B bond. Thus

$$\sqrt{E_{A-B}} \propto \text{ Amount of ionic character in A-B bond}$$

And

$$x_A - x_B \propto \text{Amount of ionic character in A-B bond}$$

Consequently:

$$x_A - x_B \propto \sqrt{E_{A-B}}$$

$$x_A\text{-}x_B = K\sqrt{E_{A-B}}$$

Now on putting the value of Δ_{A-B} from equation (i) we get

$$x_A\text{-}x_B = K[\ E_{A\text{-}B} - \sqrt{E_{A-A}} \times \sqrt{E_{A-B}}\ ]^{1/2}$$

The value of the constant, K has been found to be equal to 0.208 which comes from the conversion of experimental values of $E_{A\text{-}B}$ measured in Kcals/mole into eV. Thus:

$$x_A\text{-}x_B = 0.208\ [\ E_{A\text{-}B} - \sqrt{E_{A-A}} \times \sqrt{E_{A-B}}\ ]^{1/2}$$

This equation gives only the differences in electronegativity values. This equation can be used to calculate x value of an atom provided that x value of the other element is known. Pauling assigned an arbitrary value of **4.0** for the electronegativity of fluorine and calculated that of other elements with the help of this equation. It must be remembered that in the calculation of electronegativity values Pauling has expressed ionic-resonance energies not in kcal, but in electron volts (1 eV per bond = 23 kcal per gram bond).

The disadvantage of Pauling's scale is that bond energies are not known with any degree of accuracy for many solid elements.

Mulliken's Scale:

R.S. Mulliken (1934) has suggested that the electronegativity is related to its ionization potential and its electron affinity, since these properties of an element measure its tendency to lose its valence shell electron and to attract an extra electron respectively. Therefore an atom having a high value of ionization potential (i.e. small tendency to lose its valence-shell electron) and a high value of electron affinity (i.e. having a great tendency to attract an electron) has a high value of electronegativity.

Mulliken considers the formation of a covalent bond between two atoms A and B as follows. Suppose:
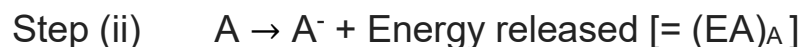
x_A and x_B = Electronegativities of atoms A and B

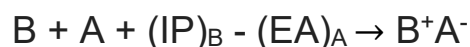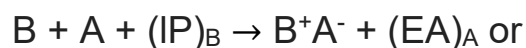$(IP)_A$ and $(IP)_B$ = Ionization potentials of atoms A and B

and $(EA)_A$ and $(EA)_B$ = Electron affinities of atoms A and B

According to Mulliken:

(i)   If $x_A > x_B$ then A^-B^+ structure will be obtained and its formation can be regarded as taking place through the following steps;

Step (i)   B + Energy supplied [= $(IP)_B$] $\rightarrow B^+$

Step (ii) $A \rightarrow A^-$ + Energy released [= $(EA)_A$]

On adding:

B + A + $(IP)_B \rightarrow B^+A^-$ + $(EA)_A$ or

B + A + $(IP)_B$ - $(EA)_A \rightarrow B^+A^-$

Energy change in the formation of B^+A^- structure

= $(IP)_B$ - $(EA)_A$

(ii)   If $x_B > x_A$, the A^+B^- structure will be obtained and the change in energy in its formation = $(IP)_A$ - $(EA)_B$

Quite obviously in the formation of a covalent bond between A and B i.e. in the formation of A-B structure) x_A will be equal to x_B and the energy changes shown above for B^+A^- and A^+B^- structures must be equal, i.e.,

$(IP)_B$- $(EA)_A$= $(IP)_A$- $(EA)_B$

or $(IP)_A$+ $(EA)_A$= $(IP)_B$+ $(EA)_B$ **...(i)**

On the basis of relation (i) Mulliken proposed that the electronegativity of an atom can be taken to be equal to the average of its IP and EA values, i.e.,

$$\mathbf{x_A} = \frac{\mathbf{(IP)_A + (EA)_A}}{\mathbf{2}} \qquad ... ii$$

Relation (ii) holds good when IP and EA of the element are given in electron volts. If these quantities are given in kilo calories, then the value of x_A is obtained by dividing the right hand side of equation (ii) by 62.5. Thus :
.⎯

$$X_A = \frac{(IP)_A + (EA)A}{2 \times 62.5}$$

Mulliken's values of electronegativity are about 2.8 times as large as Pauling's values. Hence to make the Mulliken's values approximately equal to the Pauling's values, right hand side of equation (ii) is divided by 2.8. Thus :

$$X_A = \frac{(IP)_A + (EA)A}{2 \times 2.8} = \frac{(IP)_A + (EA)A}{5.6}$$

The constant 1/5.6is called **scale adjustment factor**. This factor is used when IP and EA are expressed in electron volts.

Disadvantages:

i)   Although Mullikan's scale is less empirical than Pauling's scale, yet it suffers from a serious disadvantage that electron affinities, with the exception of a few elements, are not reliably known.

The values of ionization potential and electron affinity refer to the transfer of electrons between the atomic orbitals. However, the exact constitution of such

ii)   Atomic orbitals is not always known. Further ionization potential and electron affinity values will vary with the nature of valence state. Thus, if the valence electrons in nitrogen atom in its valence state are s2p3 (two electrons in s-orbital and three electrons in p orbitals of valency energy level), the electronegativity value comes to 2.33 while if the electrons are in sp4 state which represents the excited state of nitrogen atom one electron in s-orbital and four in p-orbitals), the electronegativity value becomes 2.55.

1.   Sanderson's Scale:

Sanderson's electronegativity scale is based on a new quantity called **stability ratio**, SR for an atom which is defined as

*" the ratio of the average electron density, **ED** (electron density differs from point to point as electrons are not evenly spaced round the nucleus) round the nucleus and its hypothetical electron density, **ED$_h$** which the atom would have, if it were an inert gas atom. Thus:*

$$\textbf{SR=} \frac{\text{ED}}{\text{ED}_\text{h}}$$

o   According to Sanderson the stability ratio (SR) of an atom, A is a measure of its electronegativity, x_A, i.e.

$$\textbf{(x}_\textbf{A}\textbf{)}_\textbf{Sanderson}\textbf{=SR=}\quad \frac{\text{ED}}{\text{ED}_\text{h}} \qquad\qquad \textbf{…(i)}$$

Equation (i) is called Sanderson's equation.

According to Sanderson ED is a measure of comparative compactness of the atom and it is obtained by dividing the number of electrons (i.e. nuclear charge (Z) round the nucleus by $\frac{4}{3}\pi r^3$, where r is the non-polar covalent radius of the atom. Thus**:**

$$\textbf{ED=} \frac{\text{Z}}{\frac{4}{3}\text{Pr3}} \textbf{=}\quad \frac{3\,\text{Z}}{4\,\text{pr3}} \quad\textbf{=}\quad \frac{\text{Z}}{4.19\,\text{r3}}$$

The value of ED_i for a particular atomic number is found from interpolation obtained by plotting electron densities of inert gas atoms against atomic numbers.

Sanderson's electronegativity values obtained by the above equation can be converted empirically to Pauling's values by using the relation:

$$\textbf{x}_\textbf{Pauling} \textbf{= 0.21 x}_\textbf{Sanderson} \textbf{+ 0.77}$$

2.   Allred and Roschow's Scale:

In 1958 Allred and Rochow suggested another scale of electronegativity which is based on covalent radii. According to this scale

"electronegativity of an atom is the force of attraction between the nucleus of an atom and an electron of an adjacent atom bonded to it and separated from the nucleus by the covalent radius."

Thus, if Z_{eff} is the effective nuclear charge, the effective nuclear charge felt by the electron under the influence of the nucleus is Z_{eff} e and the force of attraction between the nucleus and the electron is, therefore, equal to $(Z_{eff}$ e) x e/r^2, where r is the distance (in cms) between the nucleus and the

electron. This force of attraction is equal to the electronegativity, x_A of an atom A. Thus:

$$x_A = \frac{(Zeff\ e) \times e}{r2} = \frac{(Zeff\ e2)}{r2}$$

➢   In order to correlate Allred and Rochow's electronegativity values (which are absolute values) given by the above equation with Pauling's values (which are arbitrary and only relative), Allred and Rochow's values are plotted against Pauling's values and the best straight line is drawn through the points. From the slope and the intercept of this line they obtained the following relation for the electronegativity values [Allred and Rochow's values denoted by $(x_A)_{AR}$]

$$(x_A)_{AR} = 0.359\ \frac{Zeff}{r2} + 0.744$$

In this equation r is in angstrom units (A units). The value of Z_{eff} can be determined by Slatter's rules according to which $Z_{eff} = Z - \sigma$ where o is the creening constant. Thus the above equation becomes:

$$(x_A)_{AR} = 0.359\ \frac{Z - \sigma}{r2} + 0.744$$

Advantages:

Z_{eff} can be estimated by Slatter's rules and r can be determined experimentally for most elements.

It does not depend on the quantities like electron affinities and bond dissociation energies which are known for comparatively few elements.

Disadvantage:

The most serious disadvantage of this scale is that the values of covalent radii are unreliable.

None of the electronegativity scales discussed above has a distinct advantage over the others. Drago (1960), who has critically examined various proposed scales, is of the view that Pauling's scale with all its limitations is the best one.`

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

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

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

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 0 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)

Halogens (Elements of VII A group)	No. of inner shells (Complete electronic configurations are given in parenthesis)	Electronegativity
F(9)	1(2, 7)	4.0
Cl (17)	2 (2, 8, 7)	3.0
Br (35)	3(2, 8, 18. 7)	2.8
I (53)	4(2, 8, 18, 18, 7)	2.5
At (85)	5(2, 8, 18, 32, 18, 7)	2.2

←Increasing   *←Decreasing*

3. **Charge on the ion (Type of the ion)**:

A cation attracts the electron pair more readily towards itself than the atom from which it has been derived. This is due to the smaller size of the cation as compared to its parent atom (M+< M). Thus a cation, M+ has higher electronegativity than its parent atom, M (M+ > M).

If an element shows many positive oxidation states, the element in higher oxidation state has more value of electronegativity than that in the lower oxidation state. This is due to the fact that the atom in a higher positive oxidation state is smaller in size and hence has greater attraction for electrons. Thus we can say that an increase in the positive oxidation state increases the tendency of that element to attract electron pair towards itself and hence **electronegativity increases with the increase in positive oxidation state.**

Atom/cation	Atomic (covalent) radius (Å)	Oxidation state of atom/cation	Electro-negativity
Li	1.23	0	1.0
Li^+	0.60	+1	2.5
Mo	1.30	0	1.8
Mo^{4+}	0.68	+4	2.24
Mo^{6+}	0.62	+6	2.35
Fe	1.17	0	1.8
Fe^{2+}	0.76	+2	1.83
Fe^{3+}	0.64	+3	1.96
Sn	1.41	0	1.80
Sn^{2+}	1.12	+2	1.81
Sn^{4+}	0.71	+4	1.96
Pb	1.47	0	1.80
Pb^{2+}	1.20	+2	1.87
Pb^{4+}	0.84	+4	2.33

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 i different from that in PF_5 molecule in which the number and nature of the atom both to which P atom is bonded change.

5.   Ionization energy and electron affinity.

The numerical value of electronegativity of the atom of an element also depends both on the magnitude of ionization energy and electron affinity. Higher ionization 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 ionization energy and electron affinity also have higher values of electronegativity**. **For example**, the elements of group VIIA (halogens) which have the highest ionization energies and electron affinities also have the highest values of electronegativity. Similarly, the elements of group IA (alkali metals) which have the lowest ionization energies and electron affinities have the lowest values of electronegativity.

6.   **Type of hybridization**.

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

The increasing order of the magnitude of the electronegativity of carbon atom in the above hydrocarbons shows that methane is unreactive, ethylene is more reactive while acetylene is highly reactive. The highest value of electronegativity of carbon atom in acetylene also accounts for its highly acidic hydrogen atom (i.e. acidic properties of acetylene).

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 ionization energy and electron affinity of the elements. **The atoms of the elements which have higher value of ionization 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)   Ionization 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.