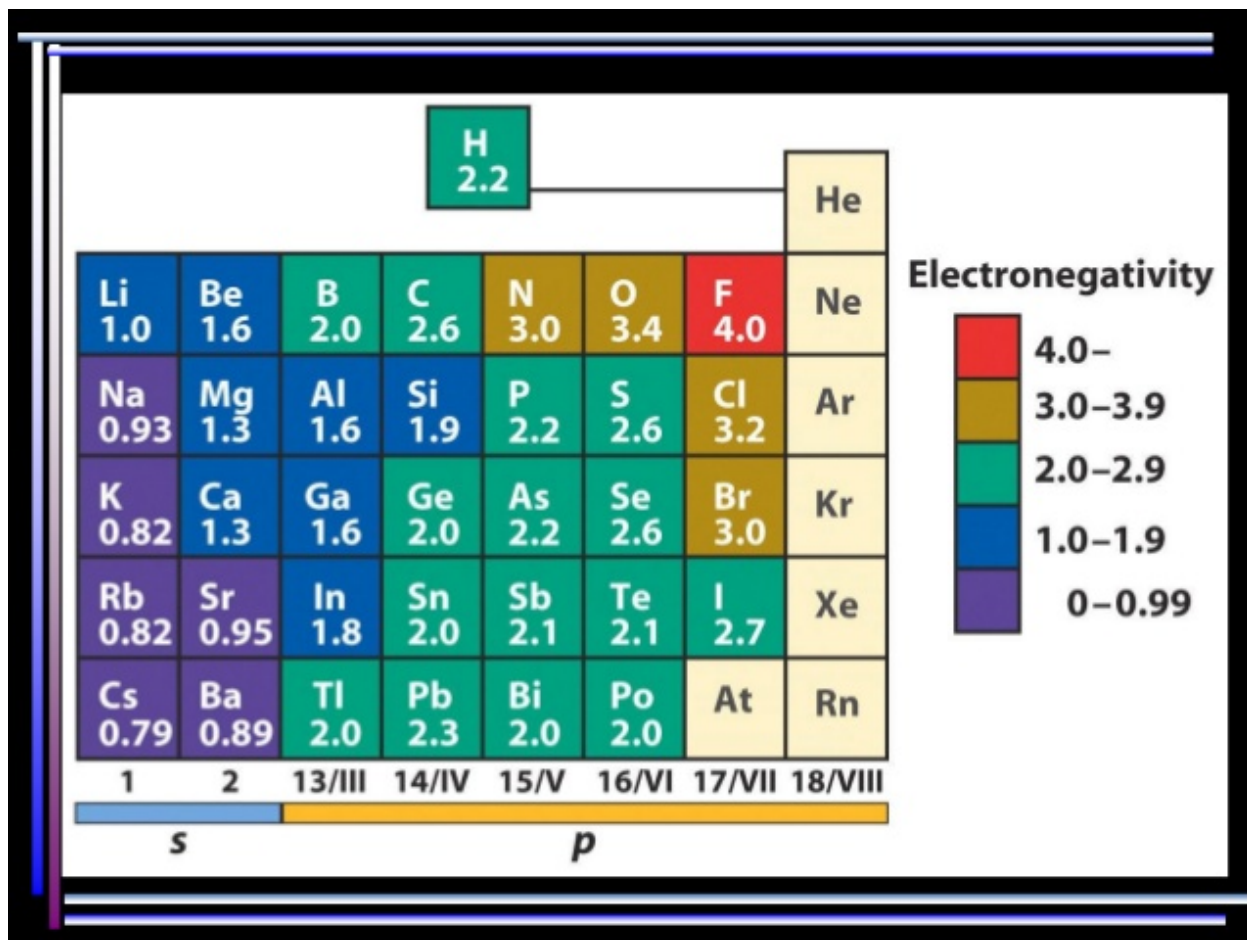


Electronegativity

Electronegativity, symbol χ , is a chemical property that describes the ability of an atom to attract electrons towards itself in a chemical bond. It is not an inherent property.

- Electronegativity cannot be directly measured and must be calculated from other atomic or molecular properties. Several methods of calculation have been proposed and, although there may be small differences in the numerical values of the electronegativity, all methods show the same periodic trend between elements.

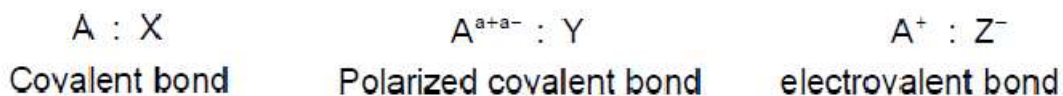
Electronegativity values of some elements (in Pauling scale):



Electronegativity gives an indication of bond type.

A bond formed between two atoms of similar electronegativity will be essentially covalent. Increase in electronegativity of one atom, will result in that atom having greater control over the bonding pair of electrons.

For example-



Electronegativity of the atoms increase in the order $x < y < z$.

Electronegativity values can be used to predict bond types:

A difference in electronegativity between two atoms of >1.7 indicates that the bond is ionic.

A difference in electronegativity between two atoms of between $0.4 - 1.7$ indicates that the bond is covalent.

Weakly Polar Covalent: An uneven share of electrons. Electronegativity difference of more than zero but less than 0.4 .

Periodicity of electronegativity values:

Values and tendencies in the periodic table: In general, the electronegativity of a non-metal is larger than that of metal. For the elements of one period the electronegativities increase from left to right across the periodic table. For the elements of one main group the electronegativities decrease from top to bottom across the periodic table.

The alkali metals possess very feeble attraction for electrons, as it is to be expected from their electronic configuration. The halogens on the other hand, have highest electronegativities in each row because of their ns^2np^5 configuration. The decrease of electronegativity down any vertical group is consistent with the variation of effective nuclear charge.

Factors influencing Electronegativity. Although the electronegativity of an element is conventionally assigned a definite value, yet it may differ from one molecule to another. The ability of an atom in a molecule to attract electrons towards itself depends upon its environment in the molecule. The electronegativity of an atom would thus depend upon the nature of the other atom with which it is attached in the molecule. The factors which largely determine the electronegativity of an atom are as follows.

Charge on the atom. An atom which acquires a positive charge, either integral or partial, would tend to attract electrons more strongly than a neutral atom. Thus, a cation will be more electronegative than the parent atom which, in turn, would be more electronegative than its anion. Also, the higher the positive oxidation state of an atom in a species, the greater would be its electron-attracting power and hence the greater would be its electronegativity. For example, the oxidation state of central chlorine atom is +1 in HClO and +5 in HClO₃. Hence, the chlorine atom will be more electronegative in HClO₃ than in HClO. Accordingly, the release of hydrogen as H⁺ ion in HClO₃ would be much easier than a similar change in HClO. In other words, HClO₃ behaves as a stronger acid than HClO.

Hybridisation. We know that *s* electrons are more penetrating than the *p* electrons. Therefore, if an atom has hybrid orbitals with a greater *s* character, the electronic charge in such orbitals would remain closer to the nucleus of that atom. This means that *the electronegativity of the atom would increase with increase in s character of its hybrid orbitals.* For example, in methane, the carbon atom involves *sp*³ hybridisation of its orbitals so that the hybrid orbitals have 25% *s* character. In ethylene, the carbon atom involves *sp*² hybridisation of its orbitals and consequently the *s* character of hybrid orbitals increases to 33%. In acetylene, the carbon atom involves *sp* hybridisation of its orbitals and, therefore, the *s* character of hybrid orbitals increases to 50%. Accordingly, the electronegativity of carbon atom increases as we move from CH₄ to C₂H₄ and to C₂H₂. Due to greater electronegativity of carbon atom in ethylene and acetylene, the electron pair of C - H bond is pulled more towards the carbon atom thereby facilitating the release of H atom as H⁺ ion. Thus, while methane is neutral, ethylene is slightly acidic while acetylene is considerably acidic.

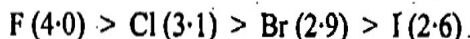
Similarly, the *basicity of amines* also varies with the type of the hybridisation of the orbitals of the nitrogen atom. The higher the *s* character of the hybrid orbitals, the greater would be the electronegativity and the lower would be the electron-donating power of the nitrogen atom and hence the lower would be the basicity of the amine. For example, the molecules RCN, C₅H₅N (pyridine) and C₆H₅NH₂, involve, respectively, *sp*, *sp*² and *sp*³ hybridisation of the orbitals of the nitrogen atom. Accordingly, the *s* character of the hybrid orbitals of nitrogen atom is 50% in RCN, 33% in pyridine and 25% in aniline. Accordingly, aniline is a stronger base than pyridine which, in turn, is a stronger base than RCN.

Effect of substituents. The electronegativity of an atom depends considerably upon the nature of the substituents attached to that atom. For example, the carbon atom in CF_3I acquires a greater positive charge than in CH_3I . Hence, the carbon atom in CF_3I is more electronegative (*i.e.*, more electron pulling) than in CH_3I . The difference in the electronegativities of an atom caused by the substituents results in different chemical behaviour of that atom. For instance, CF_3I and CH_3I yield different products on hydrolysis :

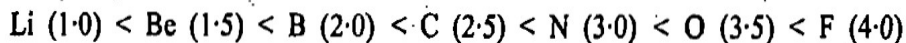


Role of ionization energies and electron affinities. According to Mulliken, electronegativity is related to the average of the ionization energy and electron affinity of the atom (Eq. 9). Evidently, the higher the ionization energy and electron affinity, the greater would be the electronegativity of the atom.

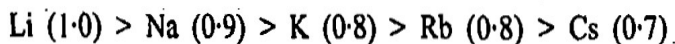
Effective nuclear charge. Variation of electronegativity in the periodic table. Allred and Rochow reasoned that the electron attracting power of an atom in a molecule is proportional to the effective nuclear charge, Z_{eff} . Thus, any factor which increases Z_{eff} , should also increase the electronegativity of the atom. For example, Z_{eff} decreases as we go down a group in the periodic table. This is because with increase in atomic number within a group, the atomic size increases. Hence, *electronegativity decreases as we move down a group*. Thus, the electronegativity of the halogens *decreases* in the order :



Z_{eff} increases with decrease in size of the atom and the size of the atom decreases as move along a period from left to right in the periodic table. Accordingly, *electronegativity goes on increasing with increase in atomic number as we move along a period*. Thus, electronegativities of the elements of the second period *increase* in the order :



Z_{eff} also depends upon the number of inner electrons which screen the last electron. The larger the number of inner electrons, the greater would be the screening and the lesser would be the effective nuclear charge. Thus, electronegativity would *decrease* with increase in the number of inner electrons in atoms of the elements in the same group. This is an additional reason why the electronegativity of alkali metals *decreases* in the order :



Applications of Electronegativities. Electronegativities have very wide range of applications. Some of the important applications are given below.

1. Calculation of partial ionic character of a covalent bond. The development of ionic character in a covalent bond between two atoms, say, A and B , is due to the difference in the electronegativities of A and B . The greater the difference in the electronegativities, the greater would be the development of *ionic character and consequently the higher would be the stability of the resulting bond*.

Pauling suggested the following correlation between the electronegativity difference $\chi_A - \chi_B$ and the per cent ionic character of the covalent bond :

$$\text{Per cent ionic character} = [1 - e^{-0.25(\chi_A - \chi_B)}] \times 100$$

2. Calculation of enthalpies of formation of compounds. It is possible to calculate enthalpies of formation of compounds from electronegativities making use of the following empirical equation put forth by Pauling :

$$\Delta H_f = 23 \epsilon (\chi_A - \chi_B)^2 - 55.4 n_N - 26.0 n_O$$

where ΔH_f is the enthalpy of formation, n_N and n_O are the numbers of nitrogen and oxygen atoms in the molecule. The value of ϵ would be 1, 2, 3, etc., depending upon the number of bonds in the molecule. For instance, $\epsilon = 1$ for HCl, $\epsilon = 2$ for BeCl_2 and so on. The values of ΔH_f obtained as above are, however, approximate.

Suppose we want to calculate the enthalpy of formation of BeCl_2 . There are two Be-Cl bonds in this molecule. The values of χ_{Cl} and χ_{Be} are, respectively, 3.1 and 1.5

$$\therefore \Delta H_f = 23 \times 2 [(3.1 - 1.5)^2] - 0 - 0 = 117.76 \text{ kcal mol}^{-1}$$

(n_N and n_O are zero since there are no nitrogen and oxygen atoms in the molecule)

(The experimental value for ΔH_f is found to be 122 kcal mol⁻¹)

3. Calculation of bond length. If the two atoms A and B bonded together through a covalent bond differ in their electronegativities, then the covalent bond would acquire some ionic character, as illustrated above. In other words, the bond acquires polarity. The greater the polarity, the shorter would be the length of the bond formed between A and B. Shoemaker and Stevenson proposed the following empirical equation for calculating the bond length in such cases :

$$d_{A-B} = r_A + r_B - 0.09 (\chi_A - \chi_B)$$

where d_{A-B} is the actual bond distance between A and B ; r_A and r_B are the covalent radii of A and B and $\chi_A - \chi_B$ is the electronegativity difference. The normal length of the covalent bond between A and B would have been equal to $r_A + r_B$. Evidently, the shortening of the bond between A and B due to electronegativity difference is equal to $0.09(\chi_A - \chi_B)$. Due to reduction in length, the bond would be more stable.

Let us calculate the bond distance N-O with the help of Eq. 14. Covalent radii of nitrogen and oxygen atoms are, respectively, 0.75 and 0.74 Å and the electronegativities of N and O are 3.0 and 3.5, respectively. Thus,

$$d_{\text{N-O}} = 0.75 + 0.74 - 0.09 (3.5 - 3.0) = 1.445 \text{ Å}$$

The actual N-O bond length is 1.46 Å

Similarly, the length of the C-O bond is given by

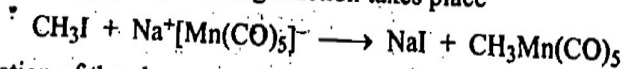
$$d_{\text{C-O}} = 0.77 + 0.74 - 0.09 (3.5 - 2.5) = 1.42 \text{ Å}$$

4. Explanation for bond angles. The lesser the electronegativity of the central atom in a polyatomic molecule, the lesser would be the magnitude of the bond angle. This may be explained as follows: If the electronegativity of the central atom is less, it would not be able to hold the bonding electron pairs towards itself. Therefore, the bonding electron pairs would shift more towards the other atoms attached to the central atom. This would result in a decrease in the bond pair-bond pair repulsion and hence a decrease in the bond angle.

For illustration, the bond angles and electronegativities of trifluorides of the Group 15 elements are given below. As expected, the decrease in electronegativity of the central atom results in a decrease of the bond angle.

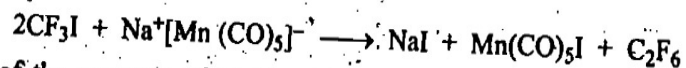
Compound	Electronegativity of Central Atom	Bond Angle
NF ₃	3.0	102°
PF ₃	2.2	97°
AsF ₃	2.2	96°
SbF ₃	2.0	88°

5. Rationalisation of reaction mechanism. It has been observed that when CH₃I reacts with the nucleophile [Mn(CO)₅]⁻, the following reaction takes place



The formation of the above reaction products may be explained as follows: Iodine in CH₃I is more electronegative than carbon. This creates a partial positive charge on the carbon atom. The negatively charged nucleophile, thus, attacks the positive site resulting in the formation of CH₃Mn(CO)₅.

On the other hand, if we carry out a similar reaction with CF₃I, a totally different product is obtained. Thus,



Because of the presence of highly electronegative F atoms, the electron charge cloud of carbon atom is pulled towards the former. This creates electron charge deficiency at the carbon atom which is made up by the pulling of the electron charge cloud of iodine atom towards the carbon atom (the electron charge cloud of iodine is easily polarisable). This creates a partial positive charge on iodine atom. Therefore, the nucleophile [Mn(CO)₅]⁻ now attacks the iodine site leading to the formation of Mn(CO)₅I.

In a similar way, we can explain the acidic or basic nature of some hydroxy compounds. Consider, for example, HOCl. The chlorine atom in this molecule is in +1 oxidation state. It is, therefore, more electron-attracting than oxygen. The chlorine atom, thus, pulls the electron pair of the O-Cl bond towards itself leaving electronic charge deficiency on the oxygen atom. In order to make up this deficiency, the oxygen atom pulls the electron pair of O-H bond towards itself. This facilitates the release of H atom as H⁺ ion by the rupture of the O-H bond. Hence, the hydroxide HO-Cl behaves as an acid.

In Be(OH)₂, the electronegativity of Be is less than that of oxygen. Therefore, the electron pair of Be-O bond is pulled more towards oxygen. This facilitates the release of OH⁻ group with the rupture of the Be-O bond. Hence, Be(OH)₂ behaves as a base.

6. Explanation of diagonal relationship. The electronegativity increases as we go from Li (1.0) to Be (1.5) (variation of electronegativity in a period) but it decreases as we move from Be (1.5) to Mg (1.3) (variation of electronegativity in a group). As a result of these two opposite changes (one along the period and the other down the group), as we move diagonally, these two effects partly cancel each other and there is no marked change in electronegativity. This is the reason why Li (1.0) and Mg (1.3) have close values of electronegativities.

Because of similar values of electronegativities and hence of electron-attracting powers, Li and Mg have similar chemical properties.

7. Types of bonds. The type of bond formed between two atoms would, evidently, depend upon the difference in their electronegativities. If this difference is zero or very small, the bond formed would be *covalent* and if the difference exceeds 2.5, the bond formed would be *electrovalent*. If, however, the electronegativity difference is less than 2.5 but otherwise quite appreciable, the bond formed would be *polar covalent*.

Scales of measurement of EN :

1. Mulliken Scale :

According to this scale, E.N of an atom is the average sum of I.E and E.A of an atom.

$$E.N = \frac{I.P + E.A}{2}$$

2. Pauling Scale :

Pauling related to resonance energy of a molecule AB with the electronegativities of the atoms A and B. If X_A and X_B are the E.N of atoms A and B respectively then,

$$0.208 \sqrt{\Delta_{AB}} = X_A - X_B \quad \text{if } X_A > X_B$$

$$\text{or } \Delta_{AB} = 23.06 (X_A - X_B)^2$$

$$\Delta_{AB} = E_{A-B} \text{ (experimental)} - E_{A-B} \text{ (theoretical)}$$

where $E_{A.B}$ is the energy of A.B bond.

In a purely covalent bond

$$E_{A-B} \text{ (theoretical)} = E_{A-B} \text{ (experimental)}$$

$$\text{So } \Delta_{AB} = 0$$

$$\text{or } 0 = 23.06 (X_A - X_B)^2$$

$$\text{or } \boxed{X_A = X_B}$$

In an ionic molecule AB, $E_{A-B} \text{ (experimental)} > E_{A-B} \text{ (theoretical)}$.

There is a relationship in between Pauling scale and Mulliken scale –

$$EN_{\text{pauling}} = \frac{EN_{\text{mulliken}}}{2.8}$$

or

$$EN_{\text{pauling}} = \frac{EA + IE}{5.6}$$

Allred and Rochow's Approach. Allred and Rochow defined **electronegativity** as the electrostatic force of attraction exerted by the nucleus of an atom on the valency electrons. Making use of the effective nuclear charge at the periphery of the atom, Z_{eff} , as calculated by Slater's rules, they proposed the following empirical relation for calculating the electronegativity :

$$\chi = 0.359 \times Z_{\text{eff}}/r^2 + 0.744$$

where χ is the electronegativity and r is the covalent radius of the atom in angstrom units. The electronegativities as calculated with the help of Eq. 8 are found to be remarkably close to those reported by Pauling.

Group electronegativity: The overall effect of charge, substituents, hybridization of the bonding orbitals etc. on the electronegativity may be summarily expressed for a group in terms of its Group electronegativity.

For example: CH_3I and CF_3I – here $-\text{CH}_3$ and $-\text{CF}_3$ group may be assigned separate overall electronegativity values. Here the electronegativity of carbon is modified by the attached H or F atoms. The values of **electronegativities of** $-\text{CH}_3$ and $-\text{CF}_3$ are 2.3 and 3.3.