Electronegativity

Electronegativity is an atomic property which is extremely important for predicting bond polarity and the course of many chemical reactions and it shows periodic variation as well. It is the tendency of an atom to pull a shared electron pair in a covalent bond towards itself. Unlike other atomic properties (example, ionisation energy, electron affinity etc.) electronegativity is not a measureable quantity and its value for an element changes with chemical environment. To quantify this tendency of an atom many scales have been proposed where electronegativity of an element varies from one scale to another. For example, Pauling scale, Mulliken scale, Allred-Rochow scale, Nagle scale, Jaffe scale, Allen scale etc. Here we will discuss few of the most frequently used electronegativity scales.

Different scales of electronegativity

1) Pauling scale

Here Pauling suggested if two molecules A_2 and B_2 react to form a product molecule, A-B, then mostly such reactions is found to be exothermic.

$$A\text{-}A + B\text{-}B \rightarrow A\text{-}B + A\text{-}B$$

According to Pauling scale, if $E_{A\text{-}B}$ is the observed bond energy of A-B molecule and E_{cov} is the hypothetical bond energy of A-B molecule where equal electron pair sharing takes place, then,

$$\left| \chi_A - \chi_A \right| = 0.102 \sqrt{\Delta} \text{ in kJ/mol}$$
$$= 0.208 \sqrt{\Delta} \text{ in kcal/mol}$$

where, $\Delta = E_{A\text{-}B} - E_{cov}$ and χ = electronegativity.

Here Δ is the ionic-covalent bond resonance energy and E_{cov} is calculated as-

$E_{cov} = (E_{A\text{-}A}.E_{B\text{-}B})^{1/2}$ where $E_{A\text{-}A}$ and $E_{B\text{-}B}$ are the covalent bond energies of A_2 and B_2 molecules respectively.

Hence, $\Delta = E_{A\text{-}B} - (E_{A\text{-}A}.E_{B\text{-}B})^{1/2}$

To calculate electronegativity values of various elements Pauling suggested electronegativity of fluorine is 4 arbitrarily.

In this Pauling's electronegativity is calculated using simple methods from where bond polarity can be well understood. But Pauling's scale suggest a single invariant electronegativity of an element irrespective of its oxidation state, state of hybridisation and nature of orbitals involved in bond formation. Also obtaining reliable bond enthalpy data is quite difficult.

Mulliken scale

In Mulliken's scale electronegativity is expressed as the intrinsic property of the element only depending upon the valence state of the atom. Here electronegativity (χ_M) is taken as the average of its ionization energy and electron affinity where both are expressed in electron volts.

$$\chi_M = (\text{Ionisation Energy} + \text{Electron Affinity})/2 \qquad \text{(both in eV)}$$

This scale of electronegativity involves a number of complicated calculations. Reliable electron affinity datas are also not available easily. This scale does not consider hybridization of the element while calculating electronegativity.

Allred-Rochow scale

According to this scale of electronegativity, electronegativity depends upon effective nuclear charge on the valence shell taking screening effect into consideration for all the electrons present in the atom and covalent radius of the atom in picometer (pm). It is expressed as

$$\chi_{AR} = [(3590Z_{eff})/r_{cov}] + 0.744$$

This scale emphasises on the fundamental properties of the element, i.e., its Z_{eff} and covalent radius and not on thermochemical data for calculating electronegativity values. Hence electronegativity of noble gases may also be calculated using this method. But this method faces difficulty in getting correct value of covalent radius.

Periodic variation

As one moves from left to right along a period, with increase in Z_{eff}, electronegativity is also found to increase gradually, as observed most prominently among s- and p-block elements. This change in d-block elements is less and among f-block elements electronegativity almost remains unchanged.

Down the group with decrease in Z_{eff} and increase in atomic size, electronegativity is usually found to decrease. But many exceptions are found due to poor screening effect of d- and f-orbitals. For example, p-block elements beyond 3d elements, i.e., Ga, Ge, As, Se and Br show higher values of electronegativity than expected due to scandide contraction.

In transition elements it is observed that electronegativity among them varies as- 3d-elements > 5d-elements > 4d-elements.

This observation may be explained in terms of poor screening effect of 4f-orbitals. As a result size of 4d and 5d-transition elements become equal. Hence Z_{eff} on 5d elements increase to a much higher value resulting in higher electronegativity.

Factors on which electronegativity depends

Electronegativity mainly depends upon oxidation state of the atom and nature of hybrid orbitals which are used for bonding.

For any particular atom, as oxidation state increases the electronegativity value also increases. For example electronegativity of metal ion varies as- Fe(III)>Fe(II); Sn(IV)>Sn(II); Tl(III)>Tl(I) etc .

Among the different atomic orbitals, tendency to penetrate varies as- s>p>d>f. Hence hybrid orbital which has higher contribution from s-orbital will experience higher Z_{eff} and hence show higher electronegativity. Thus electronegativity increases as $sp^3 < sp^2 < sp$ among hybrid orbitals with gradual increase in s-character from 25% to 50%.

Thus for hybridized orbitals, acidity increases and basicity increases with increase in s-character of hybrid orbital. For example

Acidity: CH_4 *(sp^3)* < C_2H_4 *(sp^2)* < C_2H_2 *(sp)*

Basicity: $(CH_3)_3N$ *(sp^3)* > C_5H_5N *(sp^2)* > CH_3CN *(sp)*

Again electronegativity difference among atoms or groups can vary the course of the reaction. For example:

i) $CH_3I + OH^- \rightarrow CH_3OH + I^-$

ii) $CF_3I + OH^- \rightarrow CF_3H + IO^-$

In reaction (i) –I atom is more electronegative than $–CH_3$ group. Hence OH^- reacts with $–CH_3$ group to form CH_3OH. But in reaction (ii) $–CF_3$ group is more electronegative than –I due to presence of three –F atoms. Hence OH^- now binds with I-atom in CF_3I and thereby produces OI^-. Similarly charge, substituent, hybridization etc. decide the electronegativity of a group of atoms. This is known as group electronegativity. Electronegativity of some of group of elements vary as- $CH_3<CCl_3<CF_3<NO_2$.

Knowledge of electronegativity directs us with reaction pathway as well as molecular properties like acidic nature. Hence we can predict acidity of different compounds will vary as- $HF > H_2O > NH_3 > CH_4$. But exceptions in properties of compounds or direction of a reaction may also be seen for such compounds due to other properties associated with them like lattice energy, bond energy etc.