ELECTRO NEGATIVITY

Electro negativity may be defined as the tendency (or) ability of an atom in a molecule to attract towards itself the shared pair of electron.

Variation of electro negativity in a period:

Nucleus charge increase across a period as a result of which the added electrons can be held more tightly. Thus electro negativity increase on moving from left to right in a period and attains a maximum value for the halogens.

Variation of electro negativity in a group:

In general small atoms attract electrons more strongly than large atoms. Thus electro negativity decreases with the increase in atomic size and down a group.

Electro negativity scales:

1) Pauling's scale:

Pauling establishing a scale of electro negativity based on bond energy of a hetero nuclear covalent bond.

Considered the formation of AB from A_2 and B_2 molecules.

$$A_2 + B_2 \longrightarrow 2AB$$

When AB is formed A-A and B-B bonds are broken and a new A-B bond is formed. It is found that A-B bond energy is greater than the arithmetic mean and also the geometric means of the A-A and B-B bond energies.

$$E_{A-B} > (E_{A-A} + E_{B-B})/2$$

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

According to Pauling the A-B bond is stabilized by resonance and the difference between E_{A-B} and $\sqrt{E_{A-A} \times E_{B-B}}$ is called resonance energy (Δ)

$$\Delta = E_{A-B} - \sqrt{E_{A-A} - E_{B-B}}$$

If X_A-X_B are the electro negativities of A and B, then

$$X_A - X_B = 0.088\sqrt{\Delta}$$

From this relation, the X value of one element can be calculated if that of the other is known.

Mullikan's scale:

Mullikan suggested that electronegativity of an atom is the mean of its ionization energy and electron affinity.

Electron negativity=I.E+E.A/2

Electronegativity on Pauling scale=Electronegativity on Mullikan scale/3.15

Factors affecting electro negativity:

1) size of the atom:

Smaller the size of an atom greater is its tendency to attracts the bonded pair of electrons towards itself and hence more will be its electro negativity.

2) Number of inner shells:

The atom with more number of inner shells between the nucleus and the outermost shell

Will have less electronegativity. This accounts for the decreasing order of electronegativities of halogens.

3) Oxidation states:

Elements in higher oxidation states have more electronegativity values. This is because the atom in higher oxidation state will be smaller in size and so will have greater attraction for electrons.

4) I.E and E.A:

Atoms with higher ionization energies and electrons affinities will have electrons higher electronegativity values.

Effective nuclear charge:

The effective nuclear charge is defined as the actual nuclear charge minus the shielding effect caused by the orbitals electrons.

$Z_{eff}=Z_{actual}-S$

Where Z_{actual}=nuclear charge(= atomic number)

S= sheilding constant

Calculation of S and Z effective by slater' rule:

Slater proposed a set of empirical rules to calculate the shielding constant (S) and hence the effective nuclear charge ($Z_{effective}$). Write the electronic configuration of the elements in the following order and groupings.

(1s),(2s,2p),(3s,3p),(3d),(4s,4p),(4d),(4f), (5s,5p) etc.

2) Electronic in any group to the right of the (ns, np) group contribute nothing to the shielding constant.

3) All other electrons in the same group (ns, np) group contribute 0.35 each.

4) A contribution of 0.85 per electron from all electron with (n-1) shell.

5) All electrons in the (n-2) (or) lower shells contribute 1.00 per electron.

6) All electrons in groups lying to the left of nd (or) nf group contribute 1.00 each.

Applications:

Slater's rule apply to calculate the effective nuclear charge for various electron system.

1) Nitrogen atom.

$N=7(1s^2)(2s^2,p^3)$

S=2x 0.85+ 4x0.35

S= 1.70 + 1.40 =3.1

$Z_{zeff}= Z_{actual} - S$

7– 3.1 =3.9

2) Potassium atom (n-2) (n-1) n

$K= 19=(1s^2),(2s^2,2p^6),(3s^2,3p^6),(4s^1)$

S=(10 x1.00+ 8x 0.85)

10 +6.80

=16.8

$Z_{ef} = Z_{actual}-S$

19-16.8 = 2.2

3)Chlorine atom (n-2) n-1 n

Cl=17= (1s2),(2s2,2p6), (3s2,3p5)

S= 2x 1.00+8x o.85+6x0.35

=2.00+ 6.80+ 2.10

=10.90

Z_{effect} = 17-10.90

= 6.1

4) Zinc atom n-2 n-1

Zn =30 =$(1s^2),(2s^2,2p^6),(3s^2,3p^6).(3d^{10}),(4s^2)$

S=(10x1.00)+ (18x 0.85)+(1x0.35)

S=10.00+ 15.30+0.35

S=25.65

Z_{effect}=30-25.65

=4.35