

Electronegativity:

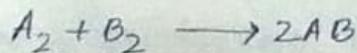
The tendency of an atom to attract bonding e^- pair towards itself is known as electronegativity.

Pauling arbitrarily chosen the electronegativity of fluorine as 4.0, which is the maximum value. EN of atoms of other elements is measured w.r.t. this ^{EN} value of F atom. To measure EN of an element different scales are proposed by different scientist. Some of its important EN scales are \rightarrow

- ① Pauling EN scale.
- ② Mulliken's EN scale.
- ③ Alfred Redshaw EN scale.

① Pauling scale: \rightarrow

Let us consider the formation of an AB and ~~at~~ AB molecule as follows



In this process the energy involved are breaking of A-A and B-B molecule and then formation of A-B molecule. If the EN of two elements A and B are same then we may consider the bond dissociation of ^{A-B} molecule is the ~~half~~ ^{dissociation} of the av. of bond dissociation of A_2 and B_2 molecule. However, because in the diff of EN

of A and B element these would not be true, because of ionic nature of the bond but in A and B it will be more stronger than a pure covalent bond.

The extra bond energy denoted by Δ will be given by $\Delta = \text{actual bond energy} - \text{energy for 100\% covalent bond}$.

This Δ is actually is the measure of EN. difference between the two elements. Pauling suggested that the 100% covalent bond energy be calculated as the C.M. of the covalent energies of ~~A-A~~ and ~~B-B~~ molecules.

$$E_{100\% \text{ covalent bond A-B}} = \sqrt{E_{A-A}} \cdot \sqrt{E_{B-B}}$$

The bond energy in A-A can be and B-B molecules can be measure and so Δ -

$$\Delta = \text{actual bond energy} - \sqrt{E_{A-A}} \cdot \sqrt{E_{B-B}}$$

Pauling states that, the EN. difference between two atoms is equal to $0.0208\sqrt{\Delta}$ where Δ is the extra bond energy in kilocal per mole. In case the measurement is done in BT. unit the EN difference would be $0.1017\sqrt{\Delta}$

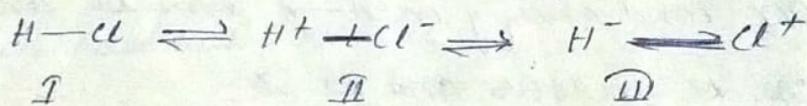
② Mulliken Electronegativity scale →

Theoretically the best process for treating EN is given by Mulliken — JAFFE system.

Mulliken suggested that two energies associated with an atom should reflect a measure of its electronegativity are:

① The ionization energy, as a measure of the difficulty of removing an e^- to form a positive species.

② The electron affinity, as a measure of the tendency of an atom to form a negative species. For eg: In the following structures



Here the structure II is stable because Cl has a high EA and H has relatively low IE for a non metal. Structure three is unstable because Cl has a high IE and H has a low EA.

Mulliken's defn of EN is given simply as

$$N = \frac{IE + EA}{2}$$

IE → Ionization energy

EA → Electron affinity

Now this expression is adjusted to Pauling scale where energies are most commonly exp

in electron-volt, $\chi_m = 0.336 \left[\frac{IE + EA}{2} - 0.615 \right]$

When the energies are expressed in MJ mol^{-1} then the expression becomes χ_m

$$\chi_m = 3.48 \left[\frac{IE + EA}{2} - 0.0602 \right]$$