Electronegativity:

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

Pauling arbitrarily choosen the electronegativity of flourine as 4.0, which is the maximum value EN of atoms of other elements is measured w.r.t. this EN value of fl atom. To measure EN of an element different scales are proposed by different scientist. Some of its important EN scales are ⟶

1. Pauling EN scale.
2. Mulikanes EN scale.
3. Alfred Rochow EN scale.

① Pauling scale :→

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

$$A_2 + B_2 \longrightarrow 2AB$$

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_2 or B_2 molecule is the ~~half of~~ the av. of bond dissociation of A–B 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 b/w A and B it will be more stronger. than a pure covalent bond.

The extra bond energy denoted by Δ will be given by Δ = actual bond energy − energy for 100% covalent bond.

This Δ is actually is the measure of EN difference b/w the two elements. Pauling suggested that the 100% covalent bond energy be calculated as the G.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 and B—B molecu 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 b/w two atoms is equal to $0.0208\sqrt{\Delta}$ where Δ is the extra bond energy in Kilocal per mole. Incase the measurement is done in S.I. unit the EN difference would be $0.1017\sqrt{\Delta}$

② Mulliken Electronegativity scale :→

Theoritically 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

$$H-Cl \rightleftharpoons H^+ + Cl^- \rightleftharpoons H^- Cl^+$$

I II III

Here the structure I is stable because Cl has a high IE and 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.

Mullikans defn of EN is given simply as

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

IE → Ionization energy

EA → Electron affinity

Hence 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 KJmol^{-1} then the expression becomes χ_m

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