

PERIODIC PROPERTIES OF ATOMS

ELECTRONEGATIVITY

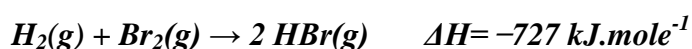
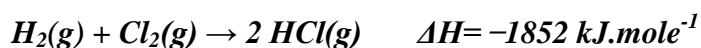
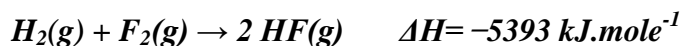
Electronegativity (X) is defined as the tendency of an atom in a covalent bond to attract the bonding electrons (or the ability to possess the electrons in the bond). In general, smaller atoms are more electronegative because they pull more electrons than large atoms. The atoms which their valence orbitals are close to fully charged have a higher electronegativity than those containing less electrons. Although the electronegativity of an atom is assumed to be constant, the electronegativity of an atom may vary as atom will have a different environment in different molecules. When we go from left to right on the periodic table, the electronegativity becomes bigger. When we go from top to bottom of the periodic table, the electronegativity decreases.

4 3,5 3 2,5 2,1 2
F, O, (N, Cl), Br (I, S, C), (H, P), B

1. Pauling electronegativity
2. Mulliken electronegativity
3. Mulliken-Jaffe electronegativity
4. Alred-Rochow electronegativity
5. Sanderson electronegativity
6. Gordy electronegativity
7. Electronegativity of functional groups
8. Allen electronegativity (spectroscopic electronegativity)
9. Hybridization and electronegativity

Pauling Electronegativity

A more widely applied quantitative treatment of electronegativity was introduced by Linus Pauling, who was an American chemist, in the early 1930s. Pauling suggested that the $A_2 + B_2 \rightarrow 2 AB$ type reaction is exothermic and the energy of the bond formed between the A and B atoms should be higher than the average bond energy of the A-A and B-B molecules.



The Pauling electronegativity value for an atom is obtained by comparing the bond energies of certain molecules containing that atom. If the bonding electrons were shared equally in a molecule AB, it would be reasonable to assume that the bond energy of AB would be the geometric mean of the bond energies of A_2 and B_2 . However, the bond energy of an AB molecule almost always is greater than the geometric mean of the bond energies of A_2 and B_2 . An example that illustrated this generalization is the HF molecule. The bond energy of HF is 565 kJ.mole^{-1} ($135 \text{ kcal.mole}^{-1}$), whereas the bond energies of H_2 and F_2 are 435 kJ.mole^{-1} ($103 \text{ kcal.mole}^{-1}$) and 155 kJ.mole^{-1} ($37 \text{ kcal.mole}^{-1}$), respectively. The geometric mean of the latter two values is 295 kJ.mole^{-1} ($62 \text{ kcal.mole}^{-1}$), which is much less than the observed bond energy of HF (565 kJ.mole^{-1}). This extra bond energy (designated Δ) in an AB molecule is assumed to be a consequence of the partial ionic character of the bond due to the electronegativity differences. The both H_2 and F_2 bonds, which are 100% covalent, are broken and 2 HF bonds are formed. If the H-F bond was also 100% covalent, the binding energy of HF would be equal to the geometric mean of the H-H and F-F bond energies.

$$\Delta H_{100\% \text{ cov}} = \frac{435 + 155}{2} = 295 \text{ kJ mol}^{-1}$$

$$\Delta X = 0.208 \sqrt{\Delta} \text{ kcal.mole}^{-1}$$

$$\Delta X = 0.1017 \sqrt{\Delta} \text{ kJ.mole}^{-1}$$

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Mulliken Electronegativity

In 1934 Mulliken proposed that the electronegativity of an atom could be defined as the geometric mean of the ionization energy and electron affinity.

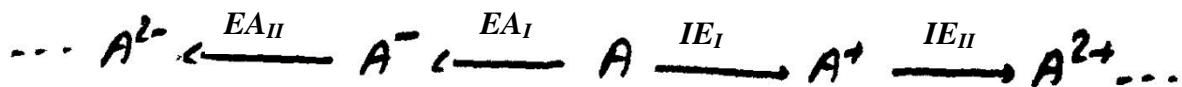
$$\chi_M = \frac{IE + EA}{2} \quad IE \text{ and } EA \rightarrow eV \text{ mol}^{-1}$$

The values found by Mulliken are about 2.8 times greater than the values found by Pauling.

$$\frac{IE + EA}{2 \times 2.8 \times 96,48} = \frac{IE + EA}{540} \quad 1eV = 96,485 \text{ kJ mol}^{-1}$$

$$\chi_P = 1,35 \chi_M^{1/2} - 1,37$$

Mulliken-Jaffe Electronegativity



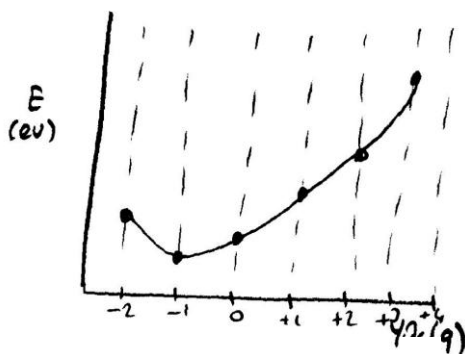
$$E_{A^{2-}} = EA_I + EA_{II}$$

$$E_{A^{-}} = EA_I \rightarrow (-)$$

$$E_{A^{+}} = IE_I$$

$$E_{A^{2+}} = IE_I + IE_{II}$$

The function of the curve obtained from the change of the energies of the ions with charge is a polynomial.



$$E = aq + bq^2 + cq^3 + dq^4$$

Total energy of atom (ΣIE or ΣEA)

$$\chi_{MJ} = \alpha + \beta q$$

$$\chi_P = 1,35 \chi_{MJ}^{1/2} - 1,37$$

$$\chi_{MJ} = \alpha + \beta q$$

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Allred-Rochow Electronegativity

In 1958, Allred and Rockow described the electronegativity of an atom as the coulomb pulling force exerted by the atomic nucleus to an electron that was as far from its covalent radius.

$$X_{AR} = F = \frac{Z^+ e \cdot e}{r^2} = \frac{Z^+ e^2}{r^2 \text{ Å}}$$

$$X_{AR} = 0,774 + \frac{0,359 Z^+}{r^2}$$

In this way, the value of 69 elements was calculated. Since the Allred-Rockow electronegativity depends on the atom's effective nuclear charge and covalent radius, the electronegativity of the atom having the highest effective nuclear charge and the smallest radius will be higher. F is the element whose electronegativity is the biggest while Cs is the element whose electronegativity is the smallest in the periodic table. The electronegativity of an atom depends on the oxidation step. As the oxidation step increases, the tendency to pull electrons and thus the electronegativity increases. As the ion charge increases in the anions, the electronegativity decreases. Allred-Rockow also calculated the electronegativity values for different oxidation steps of some elements.

Sanderson Electronegativity

In 1967, Sanderson described electronegativity as the average electron density of an atom, with the decrease in atomic size and increasing electronegativity as you go from left to right in the periodic table

$$X_S = \frac{Z}{\frac{4}{3} \pi r^3} = \frac{3Z}{4\pi r^3} \quad r = \text{Apolar covalent radius}$$

The Sanderson electronegativity calculation is quite complicated. However, the results are very close to Pauling values. Sanderson electronegativity can be converted to Pauling electronegativity.

$$X_P^{1/2} = 0,21 X_S + 0,77$$

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Gordy Electronegativity

Gordy gave the following equation by using the covalent radius of an atom with the number of valence electrons.

$$X_G = 0,31 \frac{n+1}{r} + 0,50$$

Electronegativity of Functional Groups

The electronegativity of CH_3 and CF_3 cannot be given only as the electronegativity value of C (~ 2.5). The electronegativities of these groups should be a value which includes the addition of three hydrogen or fluorine. Electronegativity values of functional groups are calculated by using dipole moment, kinetic data and electronegativities of atoms directly. In this way, $\text{CH}_3=2.3$; $\text{CF}_3=3.35$; $\text{CCl}_3=3$; $\text{CN}=3.3$; $\text{COOH}=2.85$; $\text{NO}_2=3.4$; $\text{C}_6\text{H}_5=3.0$; $\text{OH}=3.5-3.9$.

Allen Electronegativity (spectroscopic electronegativity)

Electronegativity is the average of the energies of s and p electrons in the valence shell of the atom. The E_p and E_s values in the equation result from the frequency of the lines in the atomic spectrum.

$$X_{\text{Allen}} = \frac{m E_p + n E_s}{m+n}$$

m = the number of p electrons

n = the number of s electrons

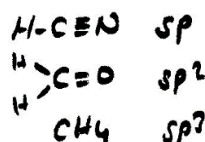
Hybridization and Electronegativity

Electronegativity can be considered as an orbital feature rather than an atomic property. Accordingly, electronegativity can be defined as the tendency of an atomic orbital to pull electrons from another atomic orbital to make bonds. s orbital is lower energy than the p orbital and is more electronegative. As the s character of the hybrid orbital increases, acidity and thus electronegativity increases.

	sp^3	sp^2	sp
χ_s	25	33,3	50
χ_c	2,5	2,75	3,29
χ_N	2,68	3,94	4,67

$\text{NH}_3 < \text{N(CH}_3)_3 < \text{N}_2$ electronegativity

$\text{NH}_3 > \text{N(CH}_3)_3 > \text{N}_2$ Alkalinity

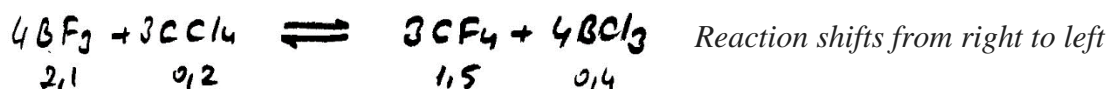
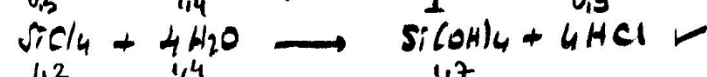
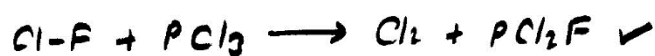
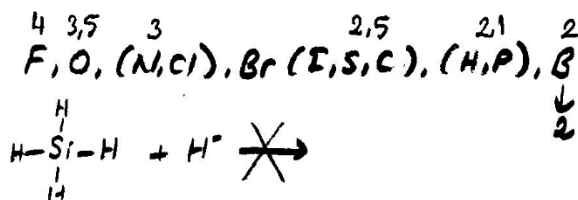


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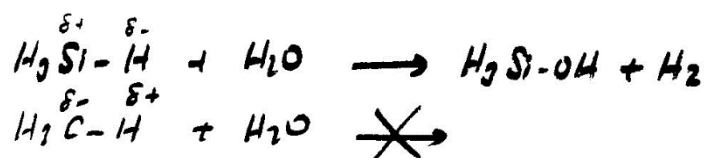
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Benefits of Electronegativity Value

- ✓ Estimating the direction of metathesis reactions. If there is an atomic exchange reaction between covalent molecules, this reaction is always in the direction of the bond with the greatest difference in electronegativity.



- ✓ Estimating whether hydrides will interact with H_2O to remove $H_2(g)$.



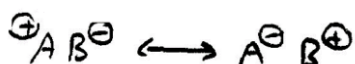
- ✓ Estimating the magnitude of the dipole moment of the molecules.
- ✓ The electronegativity of Cr^{6+} and Mn^{7+} in CrO_4^{2-} and MnO_4^- ions, respectively, is very high. So, Cr^{6+} and Mn^{7+} are absent. These ions are available wrapped with oxygen.

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Equilibrium of Electronegativity

When the two different atoms generate a bond, while more electronegative atom (B) is charged negatively, and then the more electropositive atom (A) is charged positively. In this case, the electronegativity of A increases while the electronegativity of B decreases. At equilibrium, the electronegativities of the two atoms are assumed to be equal.



$$\begin{cases} \chi_A = \alpha_A + \beta_A \delta \\ \chi_B = \alpha_B - \beta_B \delta \end{cases} \Rightarrow \delta = \frac{\alpha_B - \alpha_A}{\beta_A + \beta_B}$$

Charges of atoms are calculated here and indicates % ionic character. The second way of calculating the ionic character of a bond is the principle of equality of electronegativity. When the α and β values of H and Cl which are Mulliken-Jaffe parameters are replaced in the

$$\delta = \frac{\alpha_B - \alpha_A}{\beta_A - \beta_B}$$

relation

$$\delta = \frac{12,15 - 2,17}{11,55 + 12,84} = 0,20$$

Hannay-Smyth proposed the equation $IC\% = 16 \Delta\chi + 3,5 \Delta\chi^2$ for the calculation of the ionic character.

$$\Delta\chi = |\chi_A - \chi_B|$$

For HF,

$$\text{ionic character \% of the bond} = 16 |2,20 - 3,98| + 3,5 |2,20 - 3,98|^2 = 19\%$$

No 100% bond is present in any molecule. But there are many molecules with 100% covalent (apolar) bonds.

If %IC is > %50, the bond is ionic

If %IC is < %50, the bond is covalent

If %IC is 0, the bond is apolar covalent

If %IC is 0-50, the bond is polar covalent