Electronegativity

The tendency of an atom to attract shared pair of electrons towards itself is called electonagtivty.This definition was given by Pauling in 1932.

Electonagtivty is an inherently fundamental property of the atom and it is fundamentally different bfrom electron affinity since electron affinity represents the tendency of an isolated atom to attract the electron while electonagtivty is tendency of of a bonded to attract shared electron pair.

Sharing

if atoms bonded together have same electonagtivty the shared electrons would be equally shared.i.If the electrons of bond are more attracted to one of the atom(becouse it has more electonagtive)the electrons would be unequal shared. If the electonagtivty difference is large enough the electrons will not be shared at all .The more electonagtive atoms will take them resulting in two ions or in ionic bond

Example

Imagine the game tuq-of-war if the two teams have equal strength the rope stay center.If one team is stronger than the other team the rope is pulled in that team direction.The weaker team no longer able to hold the rope and the entire rope ends up on the side of the stronger team.This is analogous to chemical bond.

Effected by

It is effected by the

- Nuclear charge
- Number of electrons bin atomic shells

Nuclear charge

the more proton an atom has the pull it will have on the electrons.

Number of electrons in atomic shells

if an atom has more electrons further from the nucleus the valance electrons results less +ve charge they experience both becouse

- The increase distance from the nucleus
- The other electrons with low energy orbitals will act to shield the valance electrons from the positive charge nucleus.

History

- The term electonagtivty was introduced by Jons Jacob Berzelius in 1811 through the concept was known even before that and was studied by many chemists including Avogadro.
- In spite of it’s long history an accurate scale of electonagtivty was not develop until 1932.

- Then Linus Pauling proposed an electronegativity scale which depends on bond energy as development of Valance bond theory (VBT)
- It has been shown to correlate with the number of the other chemical properties.Electronagtivity can't be directly measured and must be calculated from the other atomic or molecular properties.
- Several methods of calculation have been proposed and although there may be small difference in the numerical value of the electonagtivty
- All methods show same periodic trends between the elements.

Scales for calculation of electonagtivty

The most common method used for the calculation of electonagtivty is originally proposed by Linus Pauling

Pauling scale of electonagtivty

This give a dimensionless quantity on a relative scale numbering from 0.78 to 3.98 (hydrogen=2.20).when other methods of calculation are used it is conventional to quote the results on a scale that cover the same range of numerical value this is known as electonagtivty Pauling units. As it is usually calculated

Electonagtivty is not a property of an atom alone but rather a property of atom in a molecules.

Property of atom increase

- Ionization energy
- Electron affinity

It is to be expected that the electonagtivty of an element will vary with it's chemical environmen but it is **considered a transferable property that is to say that the similar value will** be valid n a veriety it situation. Example Caesium is least electronegative in the periodic table (=0.79) and flurine is more electonagtive in the periodic table (=3.98) . Francine and caesium were both originally assigned 0.7 . caesium later refined to 0.79butbno experiment data allow to similar refinement for francium . however the ionization energy of the ceasium according with the relativistic stabilization of 7s orbitals and this fact francium is more electonagtive then the caesium.

Mulliken electronegativity scale

Robert s.Mulliken proposed that the arthemetic mean of the first ionization energy (Ei) and electron affinity (Eea) should be a measure of tendency of an atom

$$\chi = \frac{E_{\mathrm{i}} + E_{\mathrm{ea}}}{2}$$

to attract electrons.This definition is not depends on the orbitrary relative scale it has termed absolute electonagtivty with the unit kilojoules per mile or electron volt .

However it is more usual to use a linear transformation to transfer these absolute values into values that resemble the more fimilar Pauling values.For ionization energy the electron affinity in electron volts.

And for energy in kilojoules per mole.

$$\chi = (1.97 \times 10^{-3})(E_{\mathrm{i}} + E_{\mathrm{ea}}) + 0.19$$

The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known.fifty seven as of 2006.The Mulliken electronegativity of an atom is sometimes to be the positive of chemical potential . By inserting the energetic difination of the ionization energy and electron affinity into the Mulliken electronegativity bit is possible to show that the Mulliken

$$\chi = 0.187(E_{\mathrm{i}} + E_{\mathrm{ea}}) + 0.17$$

chemical potential is a finite different approximations in electronic energy with respect to the number of electrons.

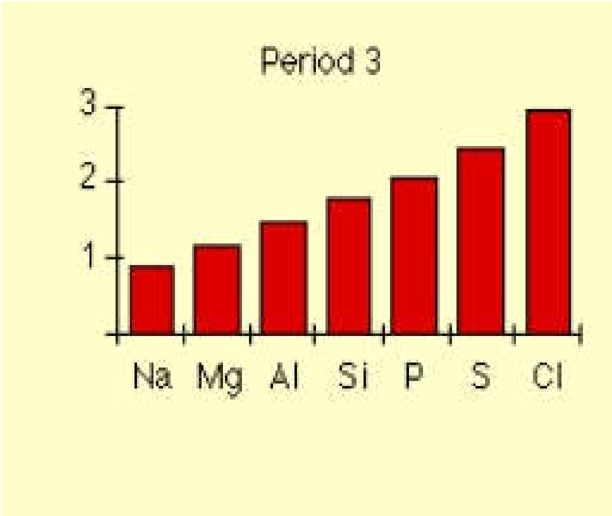
Trends in periodic table

There is different trends in periodic table in periods and groups.

$$\mu(\text{Mulliken}) = -\chi(\text{Mulliken})$$

In periods

Going from left to right the value of electonagtivty increase.This chart show electonagtivty from sodium to chlorine .we ignore argon.It don’t have electonagtivty because it doesn’t form bond.

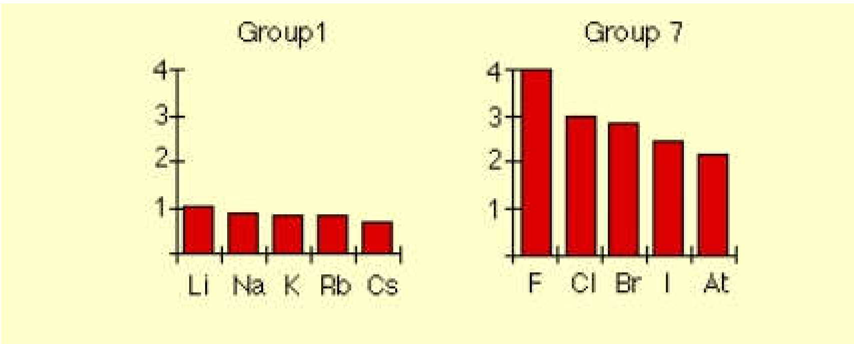


Why does electonagtivty increase across the periods?

The electonagtivty increase across the periods because number of charges on the nucleus increase .The more the charge on nucleus it attract more strongly bonding pair of electrons.

Down the groups

Going from above to down the value of electonagtivty decrease. As in group seven it is large at flurine and decrease when going down.



Why does fall moving from above to down?

Moving from above to down the value of electonagtivty decrease because the bonding pair of electrons is increasingly distant from the attraction of nucleus.

Think HF and HCl

The bonding is shared from the positive florine's nucleus only by 1s electron in the cholrine it is sheilded by all 1s,2sand 2p electrone.In each case there is a net pull the center of chlorine or florine +7.but the florine has bond pair in the two levels rather than the three levels as it is in the cholrine it is closer to the nucleus the attrrection is greater.

Variation of electonagtivty with oxidation state

In inorganic chemistry it is common to consider a single value of Electonagtivty to be valid for normal situation.but now it is clear that the electonagtivty is not an inveriable atomic property and perticularly increase with the oxidation state of the elements.

Allned used the Pauling method to calculate the electonagtivty for the different oxidation state the elements for which sufficient data was available.However for the most elements thera are not enough different covalent compound for which bond dissociation energies are known to approach feasible.This vis particularly true for the transition element where quoted electonagtivty Value are usually unassity averages over several different oxidation state.

This effect can be seen clearly in the dissociation constant of the oxiacids of cholrine.This chemical effect of this increasing electonagtivty can be seen in both in the structure of oxides and halides and in the accidty of oxiacides.This effect is much larger than could be explained by +be charge being shared among a larger no.of oxygen atom which would lead to different in PKa of log(1/4)=0.6 between hypochlorous acid and percholoric acid .The oxidation state of the centered cholrine atoms increase more electron density is drawn from the oxygen atom onto the chlorine reading the partial negative charge on the oxygen atom and increasing the accidity.

Electonagtivty and the nature of chemical bond

The concept of electonagtivty can be used to predict the nature of chemical bond formed between two similar and dissimilar atoms i.e the concept of electonagtivty can predict weather the bond between two similar and dissimilar atoms is non polar covalent,poker covalent or ionic bond.

- When $(X_a-X_b)= 1.7$ the A-B bond is 50% ionic and 50% covalent.
- When $(X_a-X_b) <1.7$ the bond is prominently covalent.
- When $(X_a-X_b)>1.7$ the bond is predominantly ionic.