7.5: Electronegativity

It is important that we be able to predict the extent to which electronic charge will be transferred from one atom to another in the formation of a chemical bond, that is, to predict its polarity. The very detailed results given previously for the charge distributions of the diatomic hydrides are not generally available and there is a need for an empirical method which will allow us to estimate the polarity of any chemical bond. It is possible to define for an element a property known as its ***electronegativity***, which provides a qualitative estimate of the degree of polarity of a bond. Electronegativity is defined as the ability of an atom in a molecule to attract electrons to itself. The concept of an electronegativity scale for the elements was proposed by Pauling.

The electron affinity of an atom provides a direct measure of the ability of an atom to attract and bind an electron:

$$X + e^- \rightarrow X^-$$

with $\Delta E = A_x$

here A_X denotes the electron affinity of atom X. For the reactions of two elements, X and Y, with free electrons, the relative values of the electron affinities A_X and A_Y provide a measure of the relative independent tendencies of X and Y to change into X^- and Y^-. However, we are interested in the reaction of X ***with*** Y and in being able to predict whether the $X-Y$ bond will be polar in the sense X^+Y^- or X^-Y^+. The electron which is to be partially or wholly gained by X or Y is not a free electron but is bound to the atom Y or X respectively. Consequently we are interested in the relative energies of the following two processes:

$$X + Y \rightarrow X^+ + Y^- \tag{7.5.1}$$

with

$$\Delta E_1 = I_X + A_Y$$

and

$$X + Y \rightarrow X^+ + Y^- \tag{7.5.2}$$

with

$$\Delta E_2 = I_Y + A_X$$

For reaction 7.5.1 to be favored over reaction 7.5.2, not only must Y have a high electron affinity, it is also necessary that X have a low ionization potential. We would expect the bonding electrons to be approximately equally shared in the $X-Y$ bond, if DE_1 = DE_2, as neither extreme structure is favored over the other. Thus the condition for a non-polar covalent bond is

$$I_X + A_Y = I_Y + A_X \tag{7.5.3}$$

or, collecting quantities for a given atom on one side of the equation,

$$I_X - A_X = I_Y - A_Y \tag{7.5.4}$$

Equation 7.5.4 states that a non-polar bond will result when the difference between the ionization potential and the electron affinity is the same for both atoms joined by the bond. If the quantity I_X - A_X is greater than I_Y - A_Y, then the product X^-Y^+ will be energetically favoured over X^+Y^-. Thus the quantity (I - A) provides a measure of the ability of an atom to attract electrons (or electronic charge density) to itself ***relative*** to some other atom. The electronegativity, denoted by the symbol χ, is defined to be proportional to this quantity:

$$\chi_x \propto I_x - A_x$$

The electronegativities of the elements in the first few rows of the periodic table are given in Table 7.5.1.

> *Thus the quantity (I - A) provides a measure of the ability of an atom to attract electrons (or electronic charge density) to itself **relative** to some other atom.*

Table 7.5.1: *Some Electronegativity Values*

H						
2.1						

H						
Li	**Be**	**B**	**C**	**N**	**O**	**P**
1.0	1.5	2.0	2.5	3.0	6.5	4.0
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	**Ca**					Br
0.8	1.0					2.8

As expected, the electronegativity increases from left to right across a given row of the periodic table and decreases down a given column. The greater the difference in the electronegativity values for two atoms, the greater should be the disparity in the extent to which the bond density is shared between the two atoms. Pauling has given empirical expressions which relate the electronegativity difference between two elements to the dipole moment and to the strength of the bond.
