Electronegativity and Bond Character

Bonds formed between atoms depend on the arrangement of electrons in the atoms and the attraction the atoms have for electrons. Since both of these characteristics are periodic properties, one can expect that the bonding of atoms occurs in a systematic way also.

Chemists have developed a comparative scale which relates the abilities of elements to attract electrons when their atoms combine. The ***Electronegativity*** of an atom is a measure of the tendency of that atom to attract electrons to itself when bound to another atom in a bond. Elements with high electronegativity have a greater tendency to attract electrons than elements with low electronegativity.

Electronegativity values are influenced by the same factors affecting ionization energies.
Values increase as one goes from left to right in a period and decrease as one descends a group. The two trends combine to give fluorine, F, the highest electronegativity and francium, Fr, the lowest Electronegativity. As a rule, nonmetals have high electronegativity values while metals have low electronegativity values. The most electronegative elements - the halogens, oxygen, nitrogen, and sulfur - are found in the upper right hand comer of the periodic table, and the least electronegative elements - the alkali metals and the alkaline earth metals are clustered near the lower left-hand corner.

Bond Character

The chemist Linus Pauling devised a method for calculating relative electronegativities of most elements (range from 0.7 to 4.0). See the periodic table in your text book for values. Bond character between two atoms depends upon electronegativity differences. The electronegativity difference is calculated by subtracting the lower value from the higher value. When the electronegativity difference is high, there is a transfer of electrons between atoms. This transfer of electrons produces ions which are then attracted to each other and form an ionic bond. Ionic bonds are formed by the transfer of electrons from a metallic element to a nonmetallic element.

If the electronegativity difference is small, then a sharing of electrons occurs and is called a covalent bond. Covalent bonds are formed by nonmetallic elements sharing two or more electrons. *At what point of electronegativity difference does the change in bond character occur?* The character of the bonds - ionic and covalent - is really on a bonding continuum, in which one type of bond fades into the next as the difference in strength between two types of atoms increases or decreases, see Table 1. In other words, nearly all bonds have both covalent and ionic characteristics. However, chemists conveniently use the electronegativity difference of 1.67 as the breaking point.

Table 1: Character of Bonds

Electronegativity Difference	0.00	0.65	0.94	1.19	1.43	1.67	1.91	2.19	2.54	3.0
% Ionic Character	0	10	20	30	40	50	60	70	80	90
% Covalent Character	100	90	80	70	60	50	40	30	20	10

If one applies the electronegativity concept to a molecule of hydrogen, H2, the Electronegativity difference between two identical atoms is zero; thus covalent – equal sharing of electrons.

Now applying this concept to HCI, the difference is 0.9, a covalent bond is formed, however the sharing of the electrons is unequal and the bonding electrons tend to spend more time closer to the more electronegative chlorine; thus resulting in a polar covalent bond. This means that the portion of the molecule in which the hydrogen atom is located has a slightly positive electrical charge, and the portion of the molecule in which the chlorine is located has a slightly negative charge. One indicates this separation of charge by using the Greek letter delta, over the appropriate portion of the molecule…

$$\overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{Cl}}$$

One can think of this unequal sharing of electrons in terms of partial transfer of electrons, or a shift in electron density from hydrogen to chlorine. This "unequal sharing" of the bonding electron pair results in a relatively greater electron density near the chlorine atom and a correspondingly lower electron density near hydrogen. The HCI bond and other polar bonds can be thought of as being intermediate between a (non-polar) covalent bond, in which the sharing of electrons is exactly equal, and an ionic bond, in which the transfer of electrons is nearly complete.

An electronegativity difference of 0.4 or less indicates that a bond is non-polar and is covalent, whilst a difference greater than 0.4 indicates that a bond is polar and covalent.

Electronegativity and electron affinity are related but different concepts. Both of these properties express the tendency of an atom to attract electrons. However, electron affinity refers to an isolated atom's attraction for an additional electron, whereas electronegativity expresses the attraction of an atom in a chemical bond i.e. with another atom for the shared electrons. Furthermore, electron affinity is an experimentally measurable quantity, whereas Electronegativity is a relative number - it is not measurable.

Classifying Chemical Bonds

1. Examine the electronegativities for the elements magnesium and oxygen. Predict the bond type.

2. Examine the electronegativities for the elements boron and nitrogen. Predict the bond type.

3. Examine the electronegativities for the elements oxygen and oxygen. Predict the bond type.

4. Classify the bonds between the following pairs of atoms as principally ionic or covalent. Show your reasoning for your answer.

a) Al + S	b) Ba + O	c) C + H	d) Li + S	e) Ca + P
f) B + Na	g) Ca + CI	h) F + S	i) Br + Rb	j) Xe + O

5. In the HI polar molecule, which atom is slightly negative? Which is slightly positive?