Chemistry
Lecture 3-4
Polarity and Intermolecular Forces

When a covalent bond forms between two nonmetal atoms, a pair of electrons is being shared between the two atoms that are bonded to each other. This sharing may or may not be equal. If the two atoms that are bonded to each other are identical as in a molecule of hydrogen, H_2, then the electrons will be shared equally and the electrons will spend most of their time exactly halfway between the two nuclei of the hydrogen atoms.

If the two nonmetal atoms that are bonded to each other are different as in the HCl molecule, then the electrons will NOT be shared equally! Different nonmetal atoms have varying degrees of attracting a shared pair of electrons. The property called <u>electronegativity</u> measures the ability of one atom to pull on the electrons it shares with another atom. Electronegativity is a periodic property that increases in the periodic table as you move left to right and bottom to top. The element with the greatest electronegativity is fluorine. You might expect helium to have the greatest electronegativity but if you will recall the noble gases do not form bonds and therefore have no electronegativity. We can see that chlorine will have a greater electronegativity than hydrogen, so the electrons being shared between the hydrogen and chlorine atoms will spend more time near the chlorine than the hydrogen. This type of bond is called a <u>polar bond</u> because the electrons are not being shared equally. The end of the bond where the electrons spend most of their time has a partial negative charge and the other end of the bond has a partial positive charge. Be sure that you do not confuse a partial charge with the charge on an ion!

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

They symbol δ is used so that you understand that the charge is a partial charge and NOT a positive or negative ion.

The bond between identical nonmetal atoms is always nonpolar due to the fact that the two atoms have the same electronegativity and thus the electrons are perfectly shared with neither end of the bond becoming partially positive or negative.

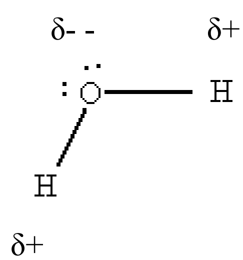
What are the requirements for a molecule to be polar, that is, to have a positive and negative end? Obviously we would guess that a molecule would have to have polar bonds to be polar! It is true that a polar molecule must have some polar bonds but it is not true that all molecules with polar bonds are polar!? How could this be?

First let's consider the carbon dioxide molecule. It is obvious that the bond between the carbon and oxygen atoms is polar. Oxygen pulls on electrons more than carbon does, so each C=O bond would have a partial positive charge on the carbon and a partial negative charge on the oxygen.

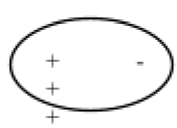
$$\overset{\delta-}{O}=\overset{\delta++}{C}=\overset{\delta-}{O}$$

Remember that the geometry of the carbon dioxide molecule is linear (2 electron domains and no unshared pairs on the central atom). The electrons in the molecule are being pulled toward the two oxygen atoms. But the oxygen atoms are on opposite sides of the carbon atom. This symmetry leads to the molecule being nonpolar even though the bonds are polar! Think of the situation where there is a tug-of-war between two teams that pull with equal forces. Nothing moves in this case! We can see that a symmetrical arrangement of polar bonds will lead to a nonpolar molecule.

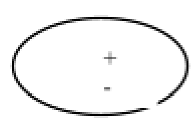
What geometries are symmetrical? Linear, trigonal planar, and tetrahedral geometries are symmetrical. Trigonal pyramid and bent geometries are NOT symmetrical due to the presence of unshared pairs of electrons. Since unshared pairs repel more than shared pairs, the symmetry of a molecule is destroyed when unshared pairs are present on the central atom. Look at the water molecule below and notice that the polar bonds are not "opposite" each other so they cannot cancel out due to the asymmetrical arrangement of the polar bonds in the bent geometry.



A polar molecule is called a dipole because it has two poles, a negative pole and a positive pole. However, please remember that a molecule is NEUTRAL! A polar molecule is neutral but it does have a positive end and a negative end. A nonpolar molecule has both its positive and negative centers of charge in the middle. Instead of drawing the entire molecule, we will represent polar and nonpolar molecules as shown below.

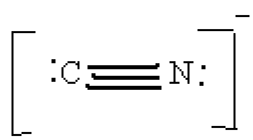


polar molecule



Nonpolar molecule

There are several ways of looking at how the electrons in a covalent bond are being shared. The formal charge on an atom sharing electrons with another atom is calculated based on the idea that the electrons are being shared equally. The calculation of formal charges completely ignores the concept of electonegativity. It is assumed that an atom owns half of the electrons it shares with other atoms and that an unshared pair belongs exclusively to one atom. The formal charge is calculated by taking the number of valence electrons in the isolated atom and subtracting the number of electrons assigned to the atom in the Lewis structure. Calculate the formal charges on the cyanide ion, CN^{-1}.

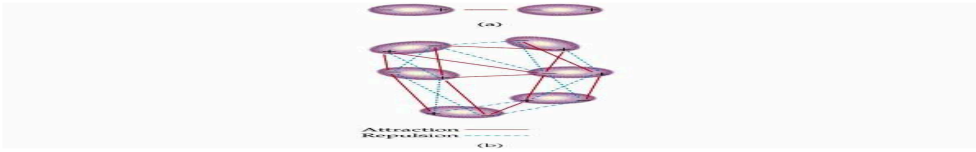


The formal charge on the carbon atom would be -1 because carbon has 4 valence electrons but in the ion it has 3 electrons that it is sharing with the nitrogen and it also has an unshared pair (4-5=-1). The formal charge on the nitrogen will be 0 since nitrogen has 5 valence electrons and it has 5 electrons in the Lewis structure. It is very important to realize that formal charges do NOT represent real charges on atoms.

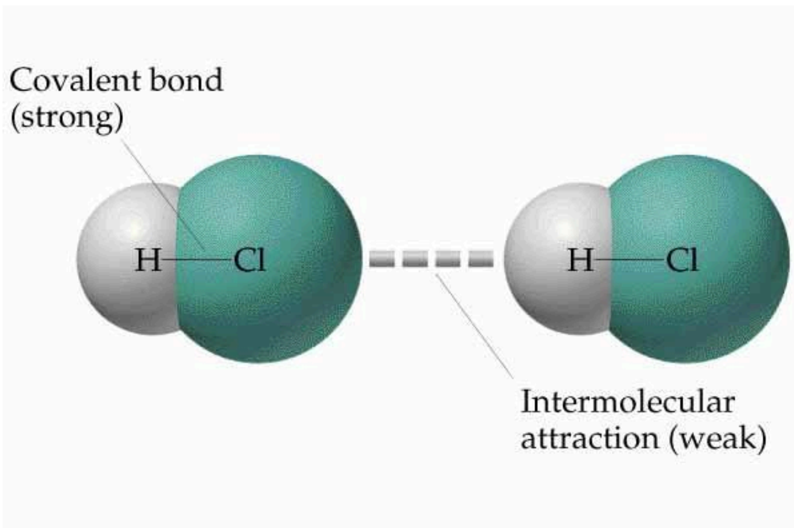
Another way of looking at the sharing of electrons between atoms is to assign oxidation numbers to the atoms sharing the electrons. When assigning oxidation numbers we assume that the electrons being shared belong completely to the atom with the higher electronegativity. In the above example we would assume that the three pairs of electrons that are being shared belong to the nitrogen since the electronegativity of nitrogen is greater than that of carbon. The oxidation number is calculated by taking the number of valence electrons in the isolated atom and subtracting the electrons in the Lewis structure assuming that one of the atoms in the bond gets all of the electrons. The oxidation number of the carbon would be +2 since the carbon would only have the unshared pair (4-2=+2). The oxidation number of the nitrogen would be -3 since the nitrogen would have 8 electrons in the Lewis structure and only 5 electrons in the isolated atom (5-8=-3).

Neither formal charges or oxidation numbers give an accurate depiction of the partial charges on the atoms in a polar bond. There is an experimental measurement called the dipole moment which can measure the fractional charges on the atoms in a polar bond or molecule. For now just remember that the dipole moment (separation of charge) will increase in size as the magnitude of the charge that is separated increases and as the distance between the charges increase.

What will happen if dipoles get near each other?



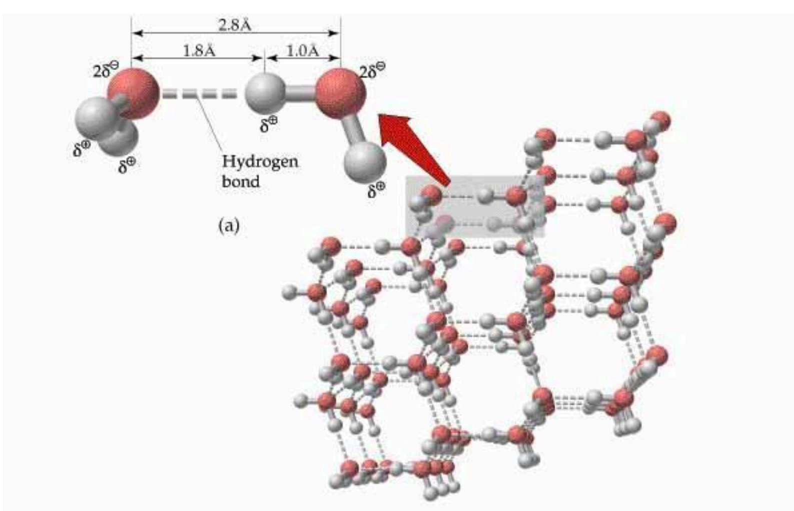
The diagram above shows that the positive end of one dipole will be attracted to the negative end of another dipole. This force of attraction is called an <u>intermolecular force</u> because it is between two different molecules. It is not a covalent bond! This particular type of intermolecular force is called a <u>dipole-dipole</u> attraction. Intermolecular forces are much weaker than covalent bonds!



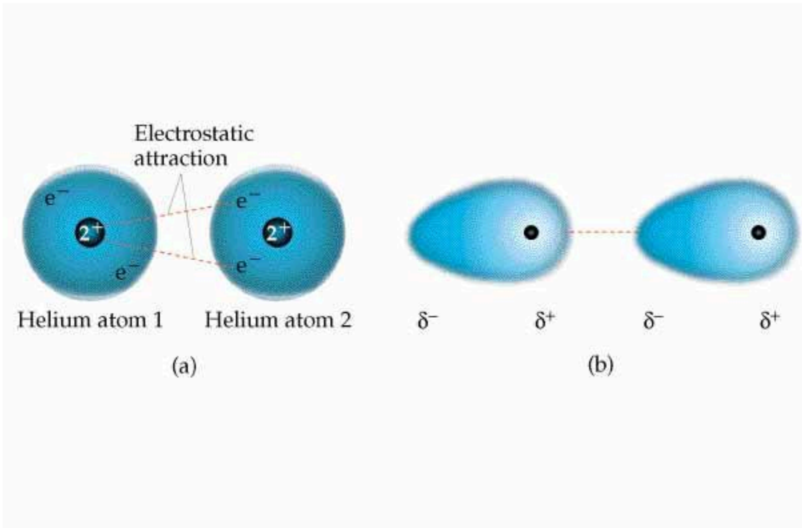
This diagram shows both the strong covalent bond that holds the H and Cl atoms together in HCl. The dotted line shows the weak intermolecular attraction that causes the polar molecules to stick to each other.

A particularly strong intermolecular force called <u>hydrogen bonding</u> occurs when a molecule contains the element hydrogen bonded to the very small and electronegative elements oxygen, nitrogen, and fluorine. Hydrogen bonding is the strongest type of intermolecular force and is responsible for the unusual properties of water. The strength of the hydrogen bond is due to the fact that when highly electronegative atoms like O, F, or N are bonded to hydrogen which has only one electron, the hydrogen end of the bond is almost a bare proton. The charge density is very high due to the small size of the hydrogen atom.

This diagram shows how the hydrogen bonding in water creates an hexagonal arrangement of water molecules in ice. This very open arrangement of molecules is responsible for the unusual property that ice is less dense than water. Usually the solid state is more dense than the liquid state. In the case of water with its hydrogen bonding, ice is less dense than water.

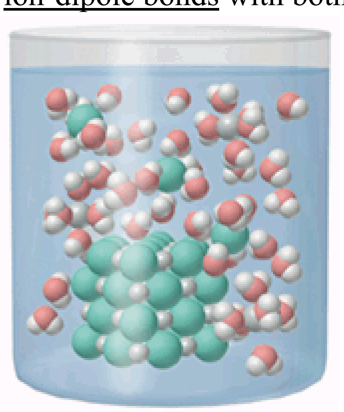


Can nonpolar molecules attract each other? Nonpolar substances like hydrogen and oxygen gases can be liquefied which indicates that the molecules must attract each other. The force that holds nonpolar molecules together is called a London dispersion force. The diagram below shows the formation of instantaneous dipoles on two adjacent He atoms. These instantaneous dipoles are the result of the electrons in a molecule being unevenly distributed around the nucleus. These temporary dipoles induce surrounding molecules to become slightly polar. These dispersion forces are the weakest type of intermolecular forces. They only operate over very short distances. Dispersion forces tend to increase in strength with increasing molecular mass. This is due to the fact that larger molecules contain more electrons with a larger electron cloud which leads to a greater change of an uneven distribution of electrons.

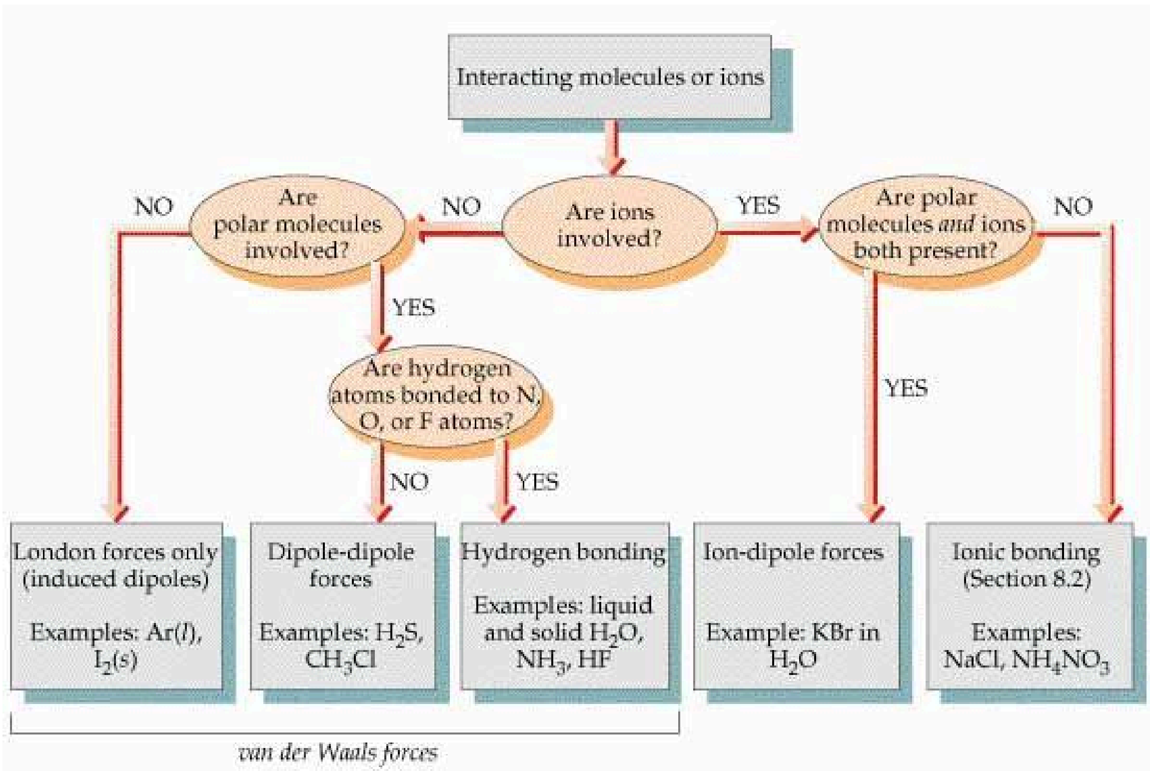


It is important to understand the dispersion forces are present in all molecules. If the molecule is also polar or can form hydrogen bonds, then these stronger intermolecular forces may be more important but the dispersion force is always present.

Molecules which are polar can be attracted to ions. When table salt is dissolved in water, the polar water molecules are attracted to both the positive sodium ions and the negative chloride ions. The diagram below shows the NaCl lattice with the positive sodium ions ionically bonded to the negative chloride ions. The polar water molecules form ion-dipole bonds with both types of ions during the dissolving process.



The flowchart below can be used to predict the types of forces holding molecules or ions to each other. Remember that London dispersion forces occur in all instances. The strength of the other forces generally increases from left to right. The three types of intermolecular forces are sometimes collectively referred to as van der Waal's forces.



Very complex mixtures of substances with varying polarities can easily be separated using chromatography. The dyes in green ink can be separated into yellow and blue components using paper chromatography. In paper chromatography the paper is the stationary phase and water is the fluid phase. A drop of green ink is placed on the paper and is allowed to dry. The green ink "sticks to" the paper because the paper is slightly polar and the blue and yellow dyes are also polar. When the strip of paper is dipped into a container of water, the water will be absorbed by the paper and move up the strip of water. The yellow and blue dyes are also attracted to the very polar water molecules. The blue dye is more attracted to the water than the paper so it will move farther up the piece of paper than the yellow dye which is more attracted to the paper than the water.

Chemistry
HW 3-4
Polarity and IMF

Name______________________________________
Period_____ Date____________________

1. Discuss how electronegativity values can be used to determine the polarity of a bond.

2. Which of the following bonds would be most polar?
   H-H, H-Cl, H-Br, H-F

3. Explain how a molecule can contain polar bonds but the molecule NOT be polar?

4. Explain why a water molecule is polar but a carbon dioxide molecule is nonpolar even though both molecules contain polar bonds?

5. Which types of molecular geometry lead to nonpolar molecules for molecules fitting the general formula AB_n?

6. What is a dipole? Explain how dipole-dipole attractions are formed.

7. What specific bond(s) must be present in a molecule for hydrogen bonding to be possible?

8. Explain how nonpolar molecules attract each other.