Intermolecular Forces and Trends in Boiling Points

Trends in boiling points are not necessarily straightforward. For example, which of the following substances has the highest boiling point?
H-Cl H-Br H-I

All three molecules are polar so relative dipole forces will important. LDF forces must also be considered in determining the relative boiling points.

In class I indicated that Cl is more electronegative than I. The electronegativity for Cl is 3.2, for I it is 2.7 and for H it is 2.2. This results in a larger dipole for HCl than for HI. However, iodine has a larger atomic radius than chlorine. There are 53 protons and 53 electrons for I and only 17 protons and 17 electrons for Cl. This results in a greater polarizability for I relative to Cl.

The trend in boiling points for HCl, HBr and HI is shown in your text, Figure 16.4, Pg. 749. It shows that HI has the higher boiling point. In this case, HCl, HBr and HI all have dipoles, but LDF forces appear to be more important in determining the boiling point than the relative dipole forces.

On the quiz today, one of the questions asked which of the following subsstances has the highest boiling point? SO_3 SO_2 CH_4 CO_2

SO_2 is bent and polar while SO_3, CH_4 and CO_2 are all non-polar. Most students indicated that SO_2 has the highest boiling point. This is a reasonable conclusion so I gave everyone credit for this answer. However, SO_3 has a higher boiling point. Why?????

The boiling points in degrees Celsius (^oC) are:

	B.P.(^oC)	Geometry	Polarity	Intermolecular Force
SO_2	– 10	bent	polar	dipole-dipole
SO_3	44.8	trigonal planar	non-polar	LDF
CH_4	– 164	tetrahedral	non-polar	LDF
CO_2	– 78.5	linear	non-polar	LDF

SO_2 is a polar molecule. Generally dipole-dipole forces are stronger than LDF forces. However, SO_3 is significantly larger than SO_2. SO_3 is also planar. LDF forces increase as the size of the molecule increases and as the surface area of contact between molecules increases. As indicated by the higher boiling point for SO_3, LDF forces for SO_3 are stronger than the dipole forces in SO_2.

LDF forces are significantly smaller for CH_4 and CO_2 relative to SO_3 due to the smaller molecular size and surface area of contact for CH_4 and CO_2 relative to SO_3.

Boiling Points versus Melting Points

Both solids and liquids are condensed phases where molecules are in close contact. Intermolecular forces are therefore more important in solids and liquids than in gases where the molecules are far apart. Vaporization of a liquid, at the boiling point, requires energy to overcome intermolecular forces of attraction between the molecules. Boiling points are therefor more indicative of the relative strength of intermolecular forces than melting points.