Intermolecular Forces of Attractions (IMFA's)

Covalent bonding, the sharing of electrons is known as an **intramolecular** force.

Intramolecular: these forces are within the molecule.

So far we have dealt mainly with these, however we will now look at **intermolecular** forces. These are the forces that exist **between** one molecule and another.

Intermolecular forces act between molecules, causing them to be attracted to each other in varying degrees. The strength of the intermolecular forces at a particular temperature determines whether a molecular substance is a gas, a liquid or a solid at that temperature.

Intermolecular forces are responsible for changes of state, and all other physical properties such as melting point, boiling point, solubility and conductivity.

Solid	→	liquid	→	gas
Strong intermolecular forces				Weak intermolecular forces

There are three principal types of intermolecular forces: dipole – dipole forces, London forces, and hydrogen bonding.

Dipole – dipole forces are between molecules with dipole moments, (i.e. with an uneven distribution of charge), London forces are often weak, but are between all types of molecules.
Collectively, they are often referred to as **van der Waals forces** after Johannes Van der Waals, a Dutch scientist who studied these forces and lived between 1837 and 1923.
However, we will refer to the individual forces using separate names.

Hydrogen bonding , the strongest type of intermolecular attraction, acts between highly polar molecules that contain hydrogen atoms bonded to very electronegative atoms.

1. The Dipole - Dipole Force

These forces exist between polar molecules, i.e. those with a permanent dipole. Whether or not a molecule is a dipole depends not only on the bond polarity but also upon the molecular geometry and the presence of lone -- pair electrons.

The partially negatively charged end of one molecule with dipole moment is electrostatically attracted to the partially positively charged part of another molecule. (That's why it is called dipole - dipole, there must be at least two molecules with dipoles !!!)

The dipole – dipole attraction must be overcome in melting a solid or vaporizing a liquid, it thereby influences the melting point, heat of fusion, boiling point, and heat of vaporization.

These forces are not that strong, only about 1% of the strength of your average covalent bond.

The strength will depend on: difference in electronegativity, i.e. strength of the dipole moment.

The following table illustrates the effect of dipole – dipole forces.

Silane, SiH_4, phosphine, PH_3, and hydrogen sulphide, H_2S, all have similar molecular mass, however silane, SiH_4 is non-polar and hence has the lowest melting point, boiling point and the lowest heats of fusion and vaporization.
Phosphine, PH_3, and hydrogen sulphide, H_2S, are both polar, however hydrogen sulphide has a dipole moment twice that of phosphine, PH_3, and thus has the highest melting point, boiling point and the highest heat of fusion and vaporization of the three compounds.

Property	**silane, SiH_4 non-polar**	**Phosphine, PH_3 polar**	**Hydrogen sulphide, H_2S polar**
Molecular mass (g mol^{-1})	32.09	34.00	34.08
Dipole moment (D)	0	0.55	1.10
Appearance	Colourless gas	colourless gas	colourless gas
Melting point (^{O}C)	– 185	– 134	– 85.6
Boiling Point (^{O}C)	– 111	– 87.8	– 60.8

2. **London Dispersion Forces** (Named after Fritz London.)

London forces act on **ALL** atoms and **ALL** molecules.

London forces is the only intermolecular force present in non-polar molecules.

London forces are responsible for the condensation, at low temperatures , of even monatomic noble gases.

Sometimes London forces are referred to as “van der Waals attractions”. Sometimes also referred to as “dispersion forces”.

London forces are the result of momentary shifts in the symmetry of the electron cloud of a molecule, i.e. the electron cloud becomes polarized. In a large collection of molecules, at any given moment collisions are taking place, with resulting polarization of the molecules.
As soon as a slight positive charge is produced at one end of one molecule, it induces a slight negative charge in one end of the molecule next to it — resulting in an induced dipole.
Thus, a temporary force of attraction exists between these molecules.

London forces are the forces of attraction due to temporarily induced dipoles in atoms and molecules that are very close together.

Since London forces are the forces of attraction between fluctuating dipoles, they are extremely weak.

The strength of London forces depends on two factors:

1. The size of the molecule, they increase with number of electrons, i.e. with increasing molecular mass.

Similar molecular geometry, increasing molecular mass :

property	methane, CH_4	silane, SiH_4
polarity	non-polar	non-polar
molecular mass (g mol^{-1})		
boiling point (^OC)	— 161	— 111

2. The geometry of the molecule, they increase with surface area of molecule:
Linear vs. branched chain molecule: a larger region gives greater opportunity for dipole interaction than when a small amount of contact is possible, (because spheres can make contact at only one point).

Same molecular mass, decreasingly compact shape:

	Pentane, C_5H_{12}	dimethylpropane, C_5H_{12}
molecular shape	$H_3C - CH_2 - CH_2 - CH_2 - CH_3$	$H_3C - C\,(CH_3)_2 — CH_3$
boiling point (^OC)	36	9.5

In each series of compounds above, the increase in boiling point is due to increasing London forces.

3. Hydrogen Bonds

This is just a special case of the dipole-dipole interaction.

This is what happens when you have BIG dipoles.

When a hydrogen atom is covalently bonded to an electronegative atom that strongly attracts the shared electron pair, the small hydrogen atom is left with very little electron density around it.

Thus, the hydrogen atom carries a small positive charge and can act as a bridge to another electronegative atom.

A **hydrogen bond** is the attraction of a hydrogen atom covalently bonded to an electronegative atom for a second electronegative atom. HCl

Strong hydrogen bonds form between hydrogen atoms and the big three highly electronegative elements: Fluorine, Oxygen , Nitrogen; which are small and have their negative charges highly concentrated in a small volume.
The hydrogen is basically stripped of its electrons leaving ________________.
This means the positive end will form an attraction to just about anything negative... like ...

Hydrogen bonds are the strongest intermolecular forces.

It is the strength of the hydrogen bonds in water that is responsible for the unique properties of water.

The hydrogen bond between hydrogen and the most electronegative element, fluorine , is the strongest type of hydrogen bond:

The effect of hydrogen bonding on the properties of compounds is clearly evident when comparing the properties of the hydrogen-bonded, second period hydrides ammonia, NH_3, water, H_2O, and hydrogen fluoride, HF, with the non-hydrogen-bonded third-period hydrides phosphine, PH_3 , hydrogen sulphide, H_2S, and hydrogen chloride, HCl:

In each of the comparable pairs from the same periodic table family:

NH_3 and PH_3 $\qquad$ H_2O and H_2S $\qquad$ HF and HCl

the compound with the smaller molecular mass is less volatile, and has the higher boiling point.
This is due to the extra energy needed to break the intermolecular hydrogen bonds in NH_3, H_2O and HF.

See Graph of Boiling Points of Hydrides of period 2, 3, and 4 versus Molar Mass

Assignment

1. What type of IMFA are found in each of the following molecules:
a. CO_2 b. $CH_2 Cl_2$ c. NH_3 d. CH_4 e. C_2H_5OH f. I_2

2. The normal boiling points of N_2, O_2, and NF_3 are –196°C, -183°C, and -129°C, respectively. Explain why the boiling point of NF_3 is substantially higher than the boiling points of nitrogen and oxygen.

3. Indicate which of the following molecular species would exhibit hydrogen bonding:
a. CH_4 b. N_2H_4 c. CH_3CH_2OH d. H_2Se e. SiH_4

4. For the following substances, determine which one has a higher melting point.
a. Xe or Neb. SbH_3 or AsH_3 c. CH_4 or C_4H_{10} d. I_2 or F_2 e. NH_3 or PH_3

5. One of the following substances is a liquid at room temperature, whereas the others are gases. Which one do you think is a liquid? Justify your answer.
CH_3OH $\qquad$ C_3H_8 $\qquad$ N_2 $\qquad$ N_2O

6. The mass of methanol (CH_3OH) is very close to that of ethane (CH_3CH_3). Which of these substances will have the higher boiling point. Explain.

7. Place the following elements in order of increasing London dispersion forces: Xe, Ar, Kr.

8. Which substance pair should have a higher melting point: (a) I_2 or Br_2, (b) O_2 or Cl_2. Justify!

9. The following fluorides of xenon have been well characterized:

XeF_2 $\qquad$ XeF_4 $\qquad$ XeF_6

Draw the Lewis structure for each, state the molecular geometry for each. Determine if each is polar or non-polar, and hence state the important intermolecular forces in each.

10. Iodine and fluorine form a series of interhalogen molecules and ions:

IF_3 $\qquad$ IF_4^{-1} $\qquad$ IF_5 $\qquad$ IF_6^{-1}

Draw the Lewis structure for each of these species. Identify the shape of the molecule or the ion. What intermolecular forces are important for each?