LECTURE 17. THEORY BEHIND INTERMOLECULAR FORCES

Intermolecular Forces – forces between molecules

- As we have just seen, there exists a correlation between the strength of the IMF and the magnitude of a property of a solution (ex. viscosity, boiling point, ΔH of vaporization, evaporation)

IMF	Strength
Instantaneous Dipoles	<1 kJ/mole
Permanent Dipoles	1-5 kJ/mole
Hydrogen Bonding	10-20 kJ/mole

Let's look more deeply at reasons for the magnitude of each of these kinds of intermolecular forces.

Permanent Dipoles

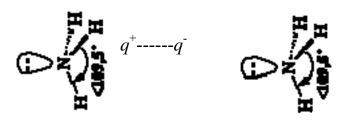
These occur in any molecule that is **not completely symmetrical**, thus, whose total electronegativity ($\sum \Delta EN$) is **not zero** (when the electronegativity values of all the species are added together).

CCl₄ does *not* have a permanent dipole; $\sum \Delta EN = 0$ and the molecule is symmetrical

CCl₃F does have a permanent dipole; $\sum \Delta EN \neq 0$ and the molecule is not symmetrical

Permanent dipoles cause intermolecular forces because each molecule possesses a q^- that has electron density and q^+ , that *lacks* electron density. As the dipoles align, $q^- - - q^+$, $q^- - - q^+$, forces are created.

Example: NH₃



Instantaneous dipoles

Symmetrical molecules possess *weak* IMF! This is why He or N₂ can be a liquid. But why does any attraction at all? Because of instantaneous dipoles.

Note the 2 electrons in Helium over time:

1 st unit of time	2 nd unit of time	3 rd unit of time	4 th unit of time
e-	e- e-		e-
++	++	++	++
e-		e- e-	e-
Instantaneous	Instantaneous	Instantaneous	Instantaneous
dipole: none	dipole: ↑	dipole: ↓	dipole: none

So although $\sum \Delta EN = 0$ over time, for an instant, dipoles are created and a weak attraction occurs.

Important Facts about instantaneous dipoles:

- 1) instantaneous dipoles are also known as London, dispersive, or Van der Waals forces
- 2) They are why noble gases form liquids and solids
- 3) Alone, they are mostly insignificant, but as the molecules increase in magnitude, dispersive forces can integrate and be quite substantial

this is why hydrocarbons are liquids at room temperature

Permanent Dipole Special Case: Hydrogen Bonds

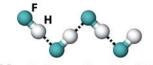
This is the strongest IMF, and is the rationale behind the phenomenon of H_2O (a molecule with a molecular weight of 18 that doesn't boil until 100° C)

In addition to the permanent dipole found in water, there is also an extremely electropositive H⁺ in the molecule.

2.1 3.0 2.1 3.5 2.1 4.0

$$H \rightarrow N \qquad H \rightarrow O \qquad H \rightarrow F \qquad q^+ \qquad q^- \qquad q^+ \qquad q^-$$

^{*}The electron density is increasingly removed from the H⁺, which results in a small, densely positive, charged region (a prime q⁺ for other molecules)

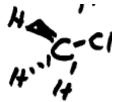


11 Hydrogen Fluoride, (HF),

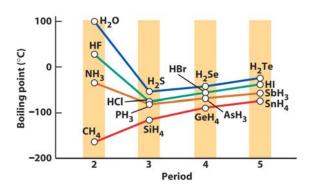
H-bonding is especially strong in the second row because of the high electronegativity values of Nitrogen, Oxygen, and Fluorine. This led to the definition of Hydrogen bonding as:

- 1) H must be involved
- 2) It must be attached to an EN atom such as N, O, F, or Cl

Thus, H₂O, HF, HCl, NH₃ have Hydrogen bonding but CH₃Cl *does not* because Chlorine is *not* attached to the Hydrogen atom

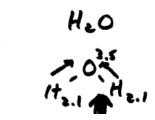


A more general definition is that Hydrogen bonding occurs for any H attached to another atom Thus, H₂S, H₂Te, and PH₃ all exhibit hydrogen bonding, though it is very weak.



One final example: IMF and Solution Properties for Ether vs. Water

Small net dipole: $\sum \Delta EN \approx 0$; slightly polar



Net dipole $\sum \Delta EN = 0$; Very Polar

Comparison of Solution Properties

		Boiling Point	Vapor Pressure	ΔΗ		
				vaporization		
Ether	Nonpolar	36° C	440 torr	226 J/g		
Water	Polar	100° C	18 torr	351 J/g		

The H₂O molecule has H bonds so:

- 1) Boiling point is larger
- 2) Vapor pressure is lower
- 3) ΔH vaporization is higher

