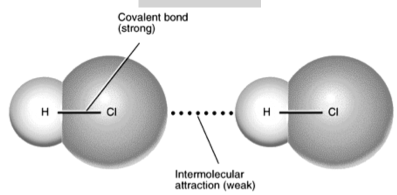
Intermolecular Forces

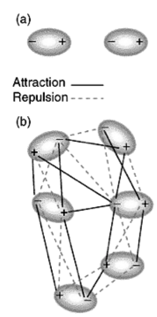
- Intermolecular forces are <u>attractive</u> forces between molecules.
  - They are <u>electrostatic</u> in nature.
- Balance of forces
  - Intermolecular forces –work to hold particles together.
  - Energy of particles – may enable particles to move relative to each other or escape attraction to other particles altogether.
    - Increases with temperature

- How do intermolecular forces act between neutral molecules?
- Recall: Many molecules are polar as a result of polar bonds whose dipole moments do not cancel each other out. One such molecule is HCl.

H - Cl
δ^{+} δ^{-}



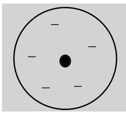
- This intermolecular force is called a <u>Dipole-Dipole force</u>.



- In the solid state, the molecules of polar substances line up in a fairly orderly arrangement as a result of these dipole-dipole attractions.
- In the liquid state, random molecular motion partially disrupts the alignment, but the attractive forces are still large enough to hold the molecules in the liquid state.

- Liquid HCl has a boiling point of -85˚C. It is estimated that ~20% of the total intermolecular forces responsible for holding HCl molecules together in the liquid state are dipole-dipole interactions. What is the other 80%? The next force we discuss.

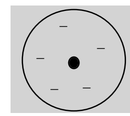
- Even non-polar atomic substances such as Ne can be liquefied at low enough temperatures (b.p. of Ne is -246˚C). What causes these atoms to stick together?



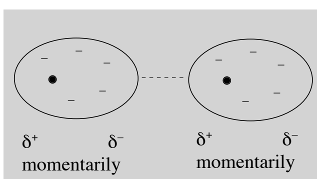
- On a time average, the electron distribution in a Ne atom is spherically symmetric. (Only 5 electrons shown for convenience.)
- However, the orbitals only describe where the probability of finding an electron is high; there is *no requirement* that the electrons always be *spread evenly* over the entire volume of the atom.

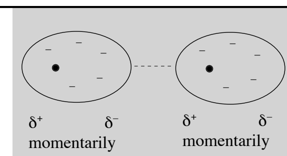
Instantaneous or momentary dipole

- Since there are a limited number of electrons, at any *instant*, more electrons may be on one side of the nucleus than the other.



- The resulting *instantaneous* dipole in one atom repels the electrons in a nearby Ne atom thus creating another dipole.

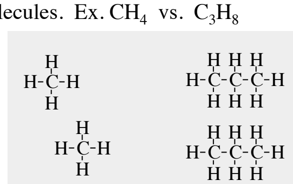




- An attraction then occurs between these *instantaneous or momentary* dipoles. This is called the London dispersion force. (Also called dispersion force or induced dipole - induced dipole.)
  - It may seem odd that as a result of electrons repelling each other, there is a net attraction but it has to do with the location of the positive charge (nucleus).

London Forces increase with

- 1. increasing molecular mass (size).
  - There are more electrons and bonds to interact with each other and generate the momentary dipoles that result in attraction between molecules. Ex. CH_4 vs. C_3H_8



London Forces increase with

- 2. larger atoms.
  - Electrons are further from the nucleus and are more easily "pushed around" to give distorted distributions that give rise to momentary dipoles. The ease with which this happens is called the polarizability or polarization of a molecule or atom.

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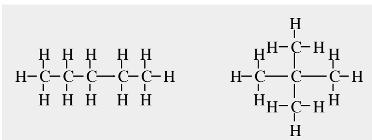
London forces increase with size and polarizability

- More compact molecules are less polarizable, i.e., they have smaller London forces. Ex. Two different compounds with formula C_5H_{12}. Discuss v.p., b.p. of two structures.



Review forces so far:

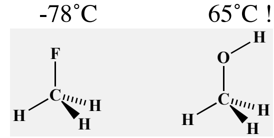
- London force, <u>Always</u> present, usually dominant
- Dipole-Dipole, significant for small polar molecules or large molecules with large dipole moments
- (Ion-Dipole), Ex. ions in aqueous solution

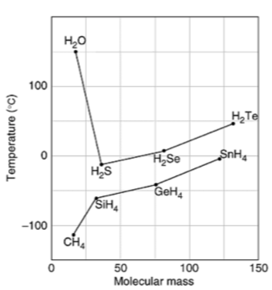
As intermolecular forces <u>increase</u>:

- Vapor pressure decreases, it is more difficult for molecules to leave the liquid
- ΔH_{vap} increases
- Boiling point increases
- Surface tension increases, it is harder to pull molecules apart to increase the surface area
- Viscosity increases, flow requires movement of molecules past each other which is slowed

One more intermolecular force

	Fluoromethane	Methanol
	CH_3F	CH_3OH
Molar Mass	34 g/mol	32 g/mol
Dipole Moment	1.81 D	1.70 D
Boiling Point	-78˚C	65˚C !





- The normal boiling point trend seems to be based on molecular mass <u>except</u> for H_2O.
  - NH_3 and HF also have unusually high boiling points compared to the other hydrides in groups 5A and 7A.

What do H_2O, NH_3, HF, and CH_3OH have in common?

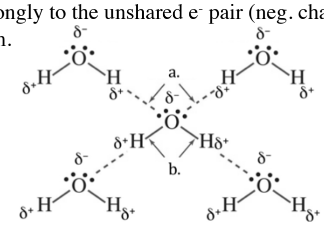
- 1. A hydrogen atom attached to a N, O, or F atom.
  - These atoms are <u>small</u> and <u>electronegative</u> or very electronegative. Both of these seem to be required. Ex. Cl has the same electronegativity as N but the boiling point of HCl is "normal".
  - Why? Because Cl is not as small as N.

What do H_2O, NH_3, HF, and CH_3OH have in common?

- 2. An unshared pair of electrons on the small, electronegative atom (in the compounds noted).
- Why doesn't CH_4 have an unusually high b.p.?
  - Carbon is not very electronegative AND, in methane, it doesn't have an unshared pair of electrons.

Hydrogen Bonds

- Hydrogen bonds are <u>MUCH</u> stronger than typical dipole-dipole forces.
  - H atoms have no core e^-s.
  - So, when the electron density is pulled away from H, what is left is a partially exposed proton which is then attracted strongly to the unshared e^- pair (neg. charge) on another atom.

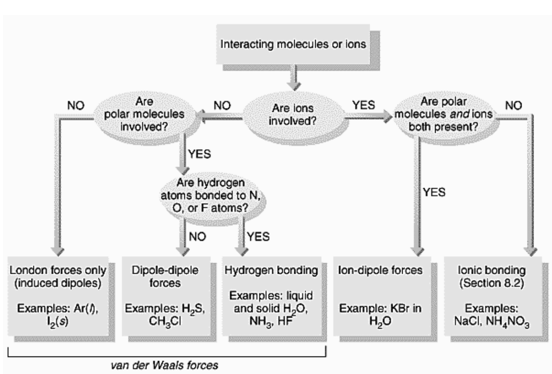


Hydrogen Bonding

- Hydrogen bonding as described here is **only** significant for O-H, N-H, and F-H bonds when the O, N, and F have an unshared pair.
- Hydrogen bonding is the strongest intermolecular force (10-40 kJ/mol). Compare to covalent bonds (150-800 kJ/mol).
- Hydrogen bonding is responsible for the uniqueness of water.

Structure of ice

- Hydrogen bonding gives ice a very "open" hexagonal structure with a lower density than that of liquid water.

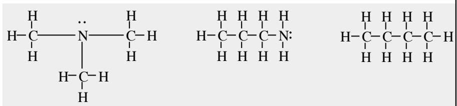


Identify the intermolecular forces in the following compounds.

- CCl_4
- CH_3Cl
- PCl_3
- $NH_4^+(aq)$

Choices
a. London forces
b. Dipole-dipole
c. Hydrogen bonding
d. Ion-dipole

Arrange the following in order of increasing boiling point.



- Formula
- Molar mass
- IMForces