

Chapter 10: Chemical Bonding II – Molecular Geometry & Intermolecular Forces**10.1: Molecular Geometry**

Molecular Structure: - the three-dimensional arrangement of atoms in a molecule.

Valence Shell Electron-Pair Repulsion (VSEPR) Model:


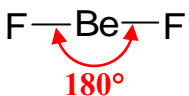
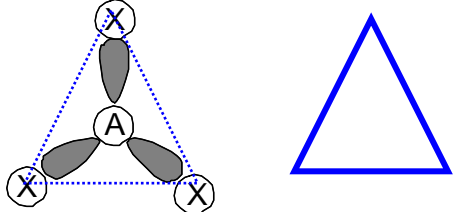
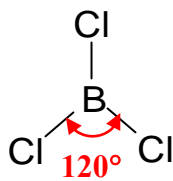
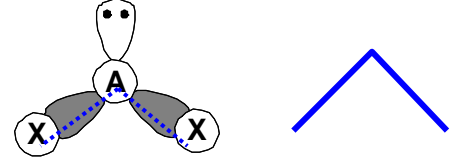
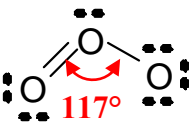
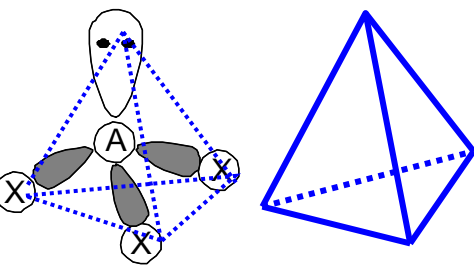
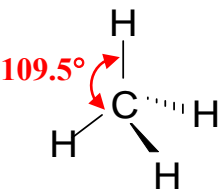
- *the best structure for a molecule is one that minimizes electrons lone pairs repulsion.*
- most often used to predict molecular structures involving non-metals.

Example: For molecules with a total of 4 e^- pairs, the bond angles decreases from 109.5° as more lone pairs added. (Repulsion of Lone Pair(s) with bond electrons pushed the angle down.)

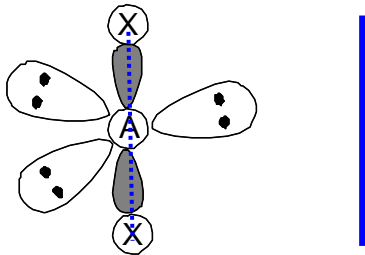
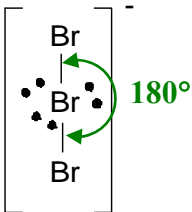
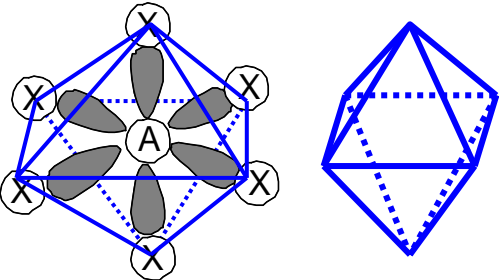
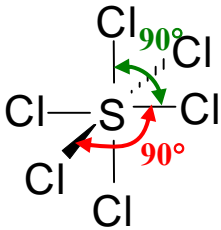
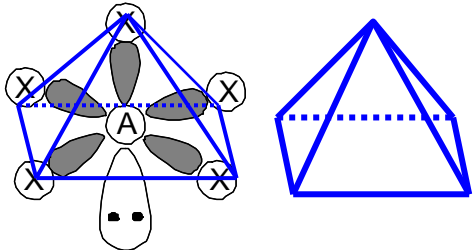
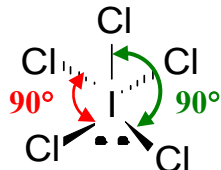
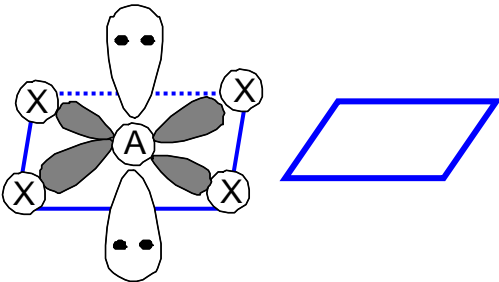
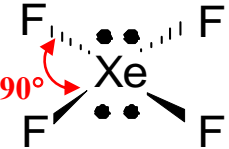
Effective Electron Pairs: - sometimes refer to as **substituents**.

- the number of lone pairs on the central atom of a molecule and the number of connections between the central atom with the outer atom(s). Each set of Multiple Bond (like double and triple bonds) count as one connection or one effective electron pair.

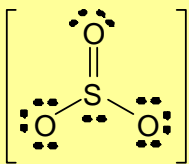
Summary of Geometrical Shape of Covalent Molecules

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
2	0		Linear	BeF_2  180°
3	0		Trigonal planar	BCl_3  120°
3	1		V-Shape (Bent)	O_3  117°
4	0		Tetrahedral	CH_4  109.5°

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
4	1		Trigonal pyramid	NH_3
4	2		V-Shape (Bent)	H_2O
5	0		Trigonal bipyramid	PF_5
5	1		See-saw	SF_4
5	2		T-Shape	ClF_3

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
5	3		Linear	Br_3^- 
6	0		Octahedral	SCl_6 
6	1		Square pyramid	ICl_5 
6	2		Square planar	XeF_4 

Example 1: From Example 2 of Sections 9.7 & 9.8, determine the geometrical shape of SO_3^{2-} . What is the possible bond angle in this polyatomic ion?

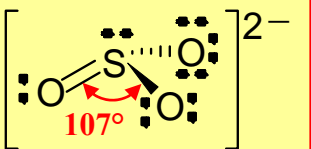


2-dimensional
Lewis structure

Around the central atom (S):

1 S = O bond (1 effective e^- pair)
 2 S - O bonds (2 effective e^- pairs)
 1 lone pair (1 effective e^- pair)

Around S, there are 4 effective e^- pairs with 1 lone pair.
(3-Dimensional Shape - Trigonal Pyramid)



**with two other
resonance structures**

Molecular Geometry of More than One Central Atom: - describe the geometry for each central atom.

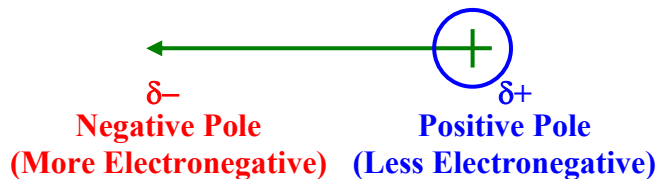
Example 2: Determine the geometrical shape of ethanol around each central atom. What are the possible bond angles in this molecule?

<p>Ethanol (C₂H₅OH) $8e^-$ (2 C atoms) $+ 6e^-$ (6 H atoms) $+ 6e^-$ (1 O atom) $20e^-$ Total $- 16e^-$ (8 bonds) $4e^-$ Left $- 4e^-$ (lone-pairs on O for octet) $0e^-$</p>		<p>Around each central atom (C), there are 4 effective e^- pairs (4 single bonds) and no lone pair.</p> <p>Around the O atom, there are 4 effective e^- pairs (2 single bonds with two lone pairs).</p>	<p>Note that the chemical formula, C₂H₅OH eludes how the atoms are arranged in the molecule.</p>	<p>(Geometrical Shape – Tetrahedral around each central C)</p> <p>(Geometrical Shape – Bent around each O)</p>
---	--	---	--	--

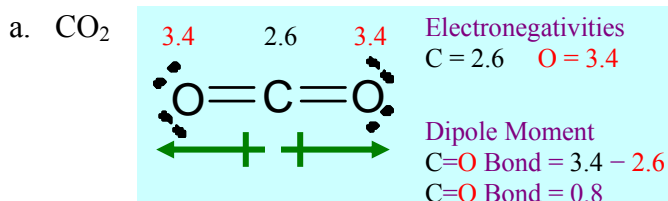
10.2: Dipole Moments

Dipole Moments (Dipolar): - the direction of the charge distribution of a polar molecule.

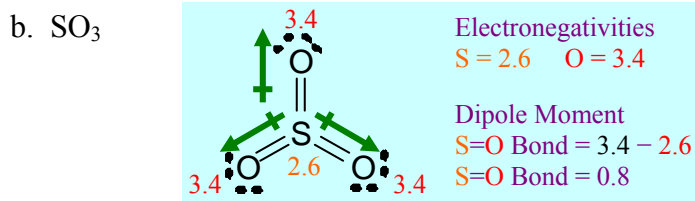
- the length of the vector indicates the strength of the relative bond polarity, whereas the arrow head indicates the direction of the higher electronegative atom (negatively shifted).



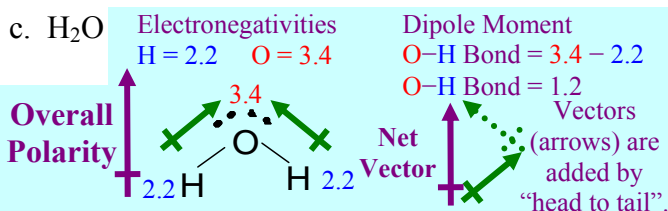
Example 1: Draw the molecular structures. Determine the dipole moments (if any) and their overall polarity of the following molecules.



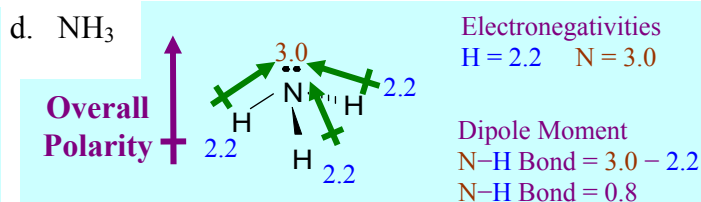
Overall, CO₂ is Non-Polar. Both dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.



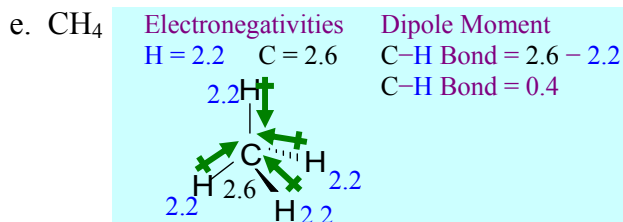
Overall, SO₃ is Non-Polar. All dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.



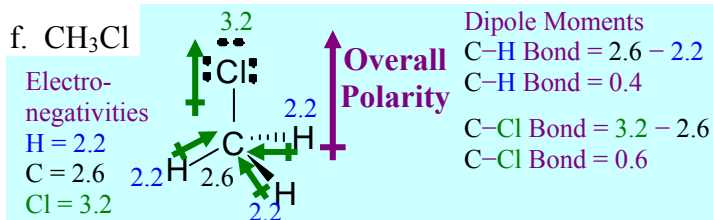
Overall, H₂O is Polar. Both dipole moments are the same, **but** there are two lone pairs on the central atom. The dipole moments do **NOT** cancel out due to the **bent** geometry of the molecule. The overall polarity of H₂O points towards the oxygen atom.



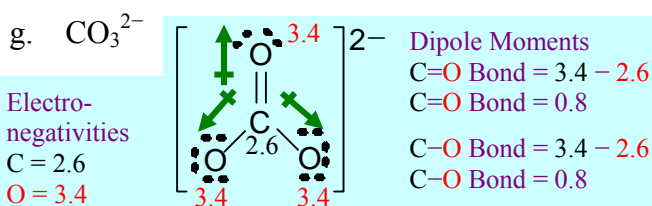
Overall, NH₃ is Polar. All dipole moments are the same, **but** there is a lone pair on the central atom. The dipole moments do **NOT** cancel out due to the **trigonal pyramid** geometry of the molecule. The overall polarity of NH₃ points towards the nitrogen atom.



Overall, CH_4 is Non-Polar. All dipole moments are the same **and** the central atom has no lone pair. Hence, the dipole moments cancel out.



Overall, CH_3Cl is Polar. The central atom has no lone pair, **but** not all dipole moments are the same (C-Cl bond has a different dipole moment than C-H bonds). The dipole moments do **NOT** cancel out even though it has a **tetrahedral** geometry. The overall polarity of CH_3Cl points towards the chlorine atom.



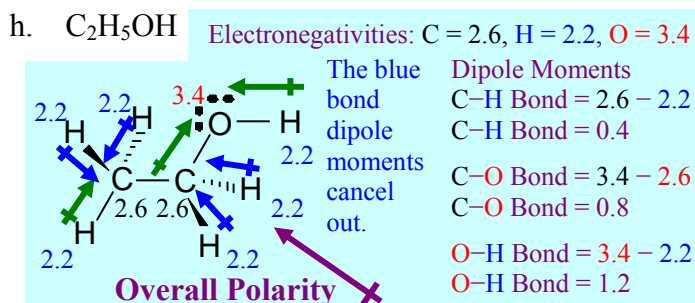
Overall, CO_3^{2-} is Non-Polar. All dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

Note: A polyatomic ion does **NOT** automatically mean that it is polar! The negative charges in this case are spread evenly over the entire structure.

Assignment

10.1 pg. 349-350 #2 to 5, 7 to 12

10.2 pg. 350 #14, 15, 20 to 22



Overall, $\text{C}_2\text{H}_5\text{OH}$ is Polar. The central C atoms have no lone pair, **but** not all dipole moments are the same (C-H bonds have a different dipole moment than C-O bond as well as O-H bond). In addition, there are two lone pairs on the oxygen atom (which can be viewed as a kind of a central atom as well). The dipole moments do **NOT** cancel out even though it has a **tetrahedral** geometry. (It **has a bent geometry** around the oxygen atom.) The overall polarity of $\text{C}_2\text{H}_5\text{OH}$ points towards the oxygen atom.

12.2: Intermolecular Forces

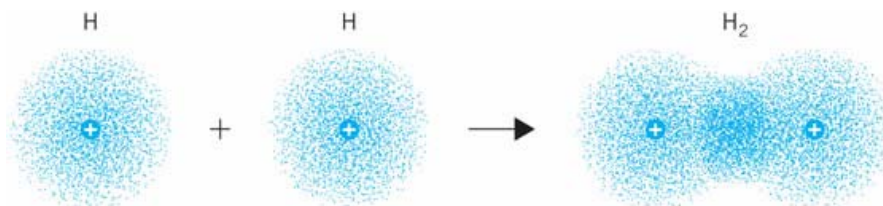
Intermolecular Forces: - attraction forces between molecules in a compound

- the strengths of the intermolecular forces **explain** the **physical properties of compounds** (solubility, boiling and freezing points).

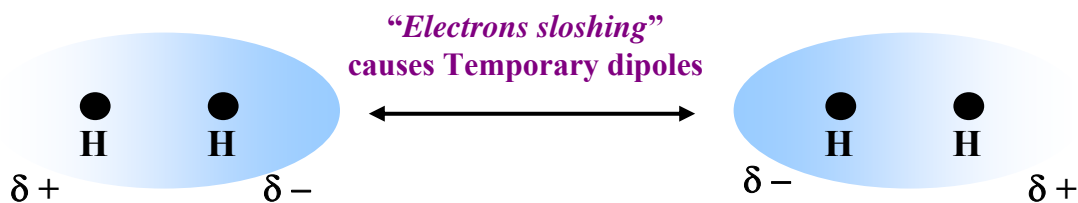
- a. **van der Waals Forces:** - Johannes van der Waals studied real gases and molecular interactions.
- there are two kinds of van der Waals forces.
 - they are **Dispersion Forces** and **Dipole-Dipole Interactions**.

- i. **Dispersion Forces:** - also known as **London Dispersion Forces** (named after Fritz London who first proposed how this force works).

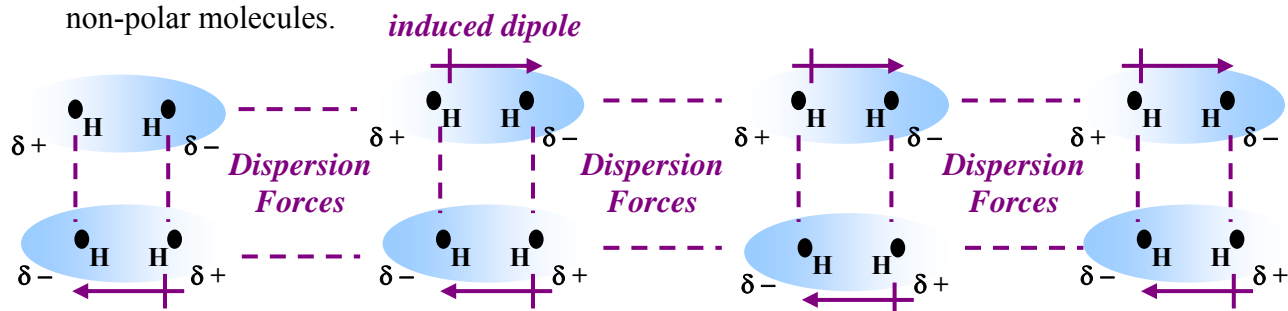
- on average, the non-polar molecules do not have any permanent dipoles like polar molecules



- the “*dispersion*” is the **temporary dipole** that forms within the molecules even in non-polar molecules due to the constant motions of electrons. In one instance, they can move to one side of the molecule making it temporary polar. In another instance, electrons will move and the direction of this temporary dipole will switch.



- This constant “sloshing around” of electrons causes non-polar molecules to have these **temporary dipoles**. These temporary “*induced*” dipoles are what cause the attractions between non-polar molecules.



- even monoatomic element like Helium has London Forces.
(Check out animation at <http://www.super-tech.ro/teoretic.html>)
- in general, *the higher the molar mass or the more electrons there are in a molecule, the stronger the London Dispersion Force* (attraction between molecules – intermolecular force). *This causes an increase in melting and boiling points of the chemical.*

-Note: All molecules have electrons. Hence, ALL molecules have London Dispersion Force.

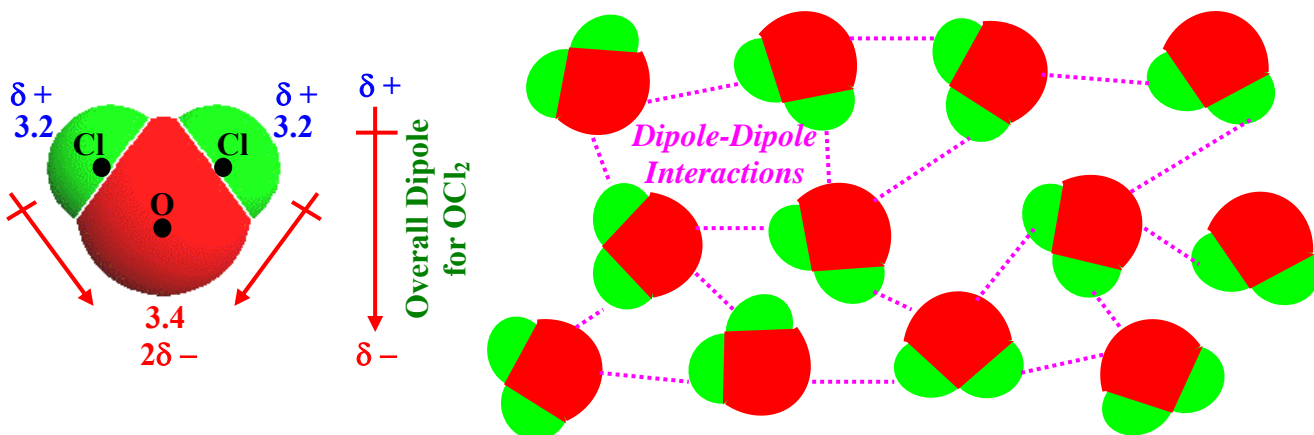
of e^- or molar mass in atom or molecule \uparrow , London Dispersion Force \uparrow , Melting and Boiling Point \uparrow

Example 1: Explain the boiling points and the melting points of the noble gases.

Noble Gases	# of e^-	Molar Mass (g/mol)	Melting Point	Boiling Point
He	2	4.00	-272°C (1 K)	-269°C (4 K)
Ne	10	20.18	-249°C (24 K)	-246°C (27 K)
Ar	18	39.95	-189°C (84 K)	-186°C (87 K)
Kr	36	83.80	-157°C (116 K)	-153°C (120 K)
Xe	54	131.29	-112°C (161 K)	-108°C (165 K)
Rn	86	222.00	-71°C (202 K)	-62°C (211 K)

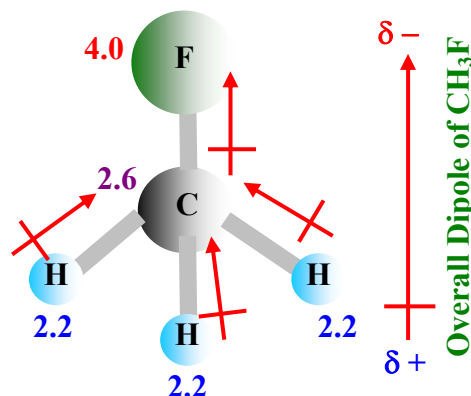
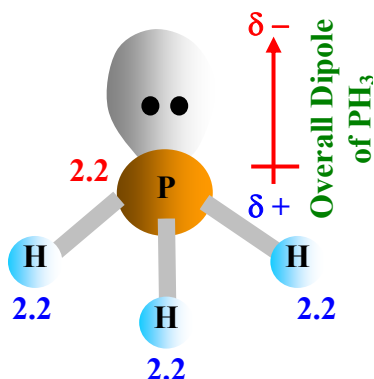
All atoms of noble gases are monoatomic non-polar. The only intermolecular force that governs the melting and boiling points is the London Dispersion Force. As the number of electrons in the noble gases increase, London dispersion force makes the attraction between the atoms greater. This in turn has an effect of increasing the boiling and melting point of the noble gas as one goes down the column.

- ii. **Dipole-Dipole Interaction**: - also known as simply **Dipole Interaction** or Dipole-Dipole Force
 - intermolecular forces resulted from polar molecules.
 - dipole interaction is **much stronger than Dispersion Force**.



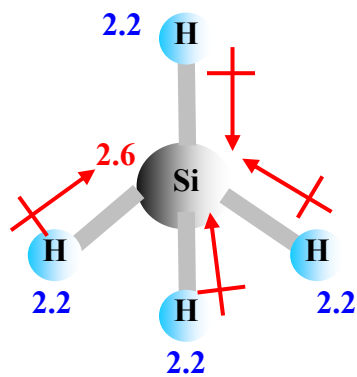
Example 2: Order the boiling points from the least to greatest for the following compounds with similar molar mass. PH_3 (34.00 g/mol), CH_3F (34.04 g/mol), and SiH_4 (32.13 g/mol)

Since PH_3 , CH_3F and SiH_4 have similar molar mass; any differences in boiling points cannot be due to London Dispersion forces. Since dipole-dipole interactions exist in polar molecules, we have to examine the molecular geometry and structure of each compound.



PH_3 has a trigonal pyramidal geometry (VSEPR) and is Polar. Even though the P–H bonds have no polarity (electronegativities of P and H are the same), the lone pair on one end of the P atom causes an uneven distribution of electrons.

CH_3F has a tetrahedral geometry and is very polar. The C–F bond along with the C–H bonds has strong polarity. The overall dipole moment for the molecule has electrons around the F atom.

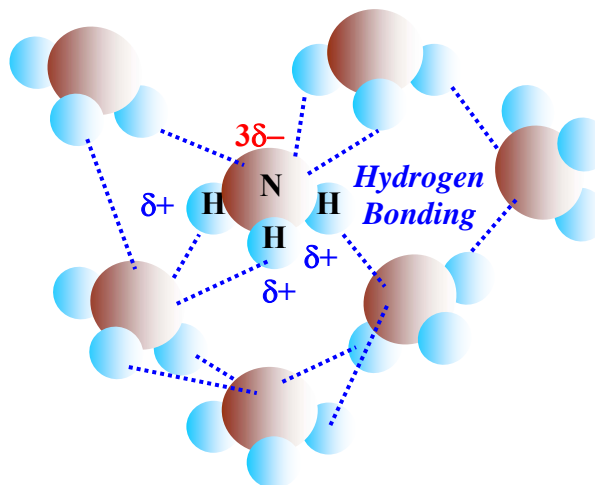
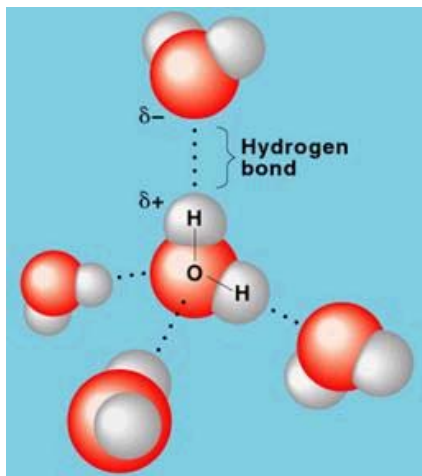


SiH_4 has a tetrahedral geometry with equal dipoles of Si–H bonds cancels out all bond polarities. Hence, SiH_4 is Non-Polar.

Since non-polar molecules have no dipole interactions, SiH_4 should have the lowest boiling point. PH_3 is less polar than CH_3F due to the difference in electronegativities between P–H bond and C–F with C–H bonds. Therefore, CH_3F must have the highest boiling point.

Boiling Point: $\text{SiH}_4 < \text{PH}_3 < \text{CH}_3\text{F}$

- b. **Hydrogen Bonds**: - are intermolecular bonds that involve **hydrogen atom with very electronegative atom that also consists of lone pairs**.
- these include **O–H, N–H, and H–Cl and H–F bonds**.
 - the resulting molecule is always polar. Therefore, **all hydrogen bonding molecules also have dipole interactions**.
 - hydrogen bond is the **STRONGEST** of the intermolecular bonds **amongst molecular compounds**.



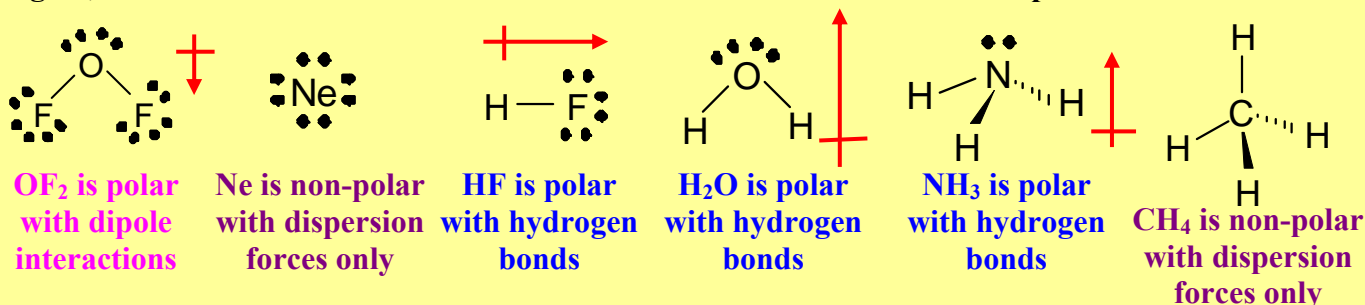
(Check out the Hydrogen Bond Animation at

<http://www.northland.cc.mn.us/biology/Biology111/animations/hydrogenbonds.html>)

Example 3: Account for the differences in the boiling points of the compounds listed below.

Molecule	Molar Mass (g/mol)	London Dispersion Forces	Dipole Interactions	Hydrogen Bonds	Boiling Point
OF ₂	54.00	✓	✓	✗	–145°C (128 K)
Ne	20.18	✓	✗	✗	–246°C (27 K)
HF	20.01	✓	✓	✓	19°C (292 K)
H ₂ O	18.02	✓	✓	✓	100°C (373 K)
NH ₃	17.04	✓	✓	✓	–33°C (240 K)
CH ₄	16.05	✓	✗	✗	–161°C (112 K)

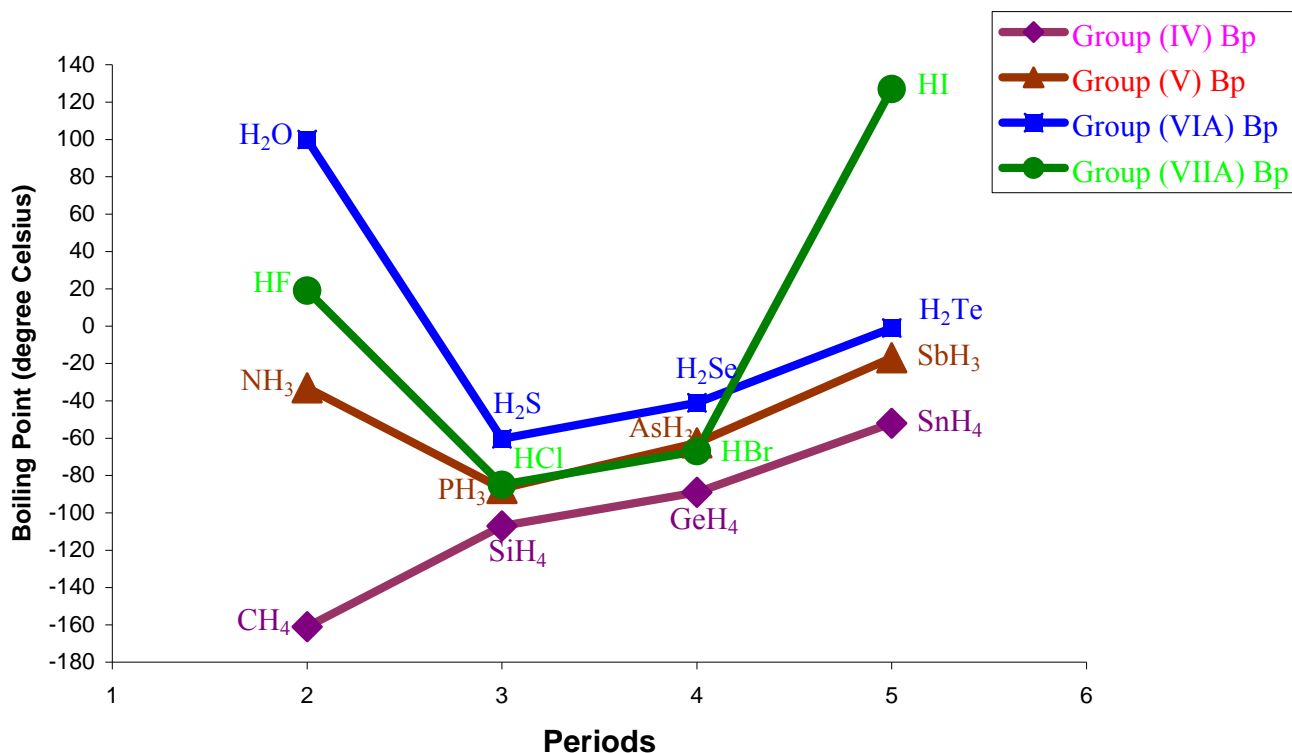
Again, we need to draw the structural formulas of these molecules and compare their polarities.



Notice that the **hydrogen bond** molecules (HF, H₂O and NH₃) have **boiling points much higher than molecule with just dipole interactions (OF₂) and the ones with only London Dispersion Forces (Ne and CH₄)**.

Example 4: Given the graph below on the boiling points of hydrogen compounds with different group series, explain the following using the concepts of chemical bonding.

Boiling Point of Hydrogen Compounds



- The hydrogen compounds in the Group (VIA) series have higher boiling points than hydrogen compounds in the other series.
- The first hydrogen compounds in Groups (VA), (VIA) and (VIIA), namely NH₃, H₂O and HF, have higher boiling points than most other hydrogen compounds in their respective series. On the other hand CH₄ has a lowest boiling point in its own Group (IVA) series.

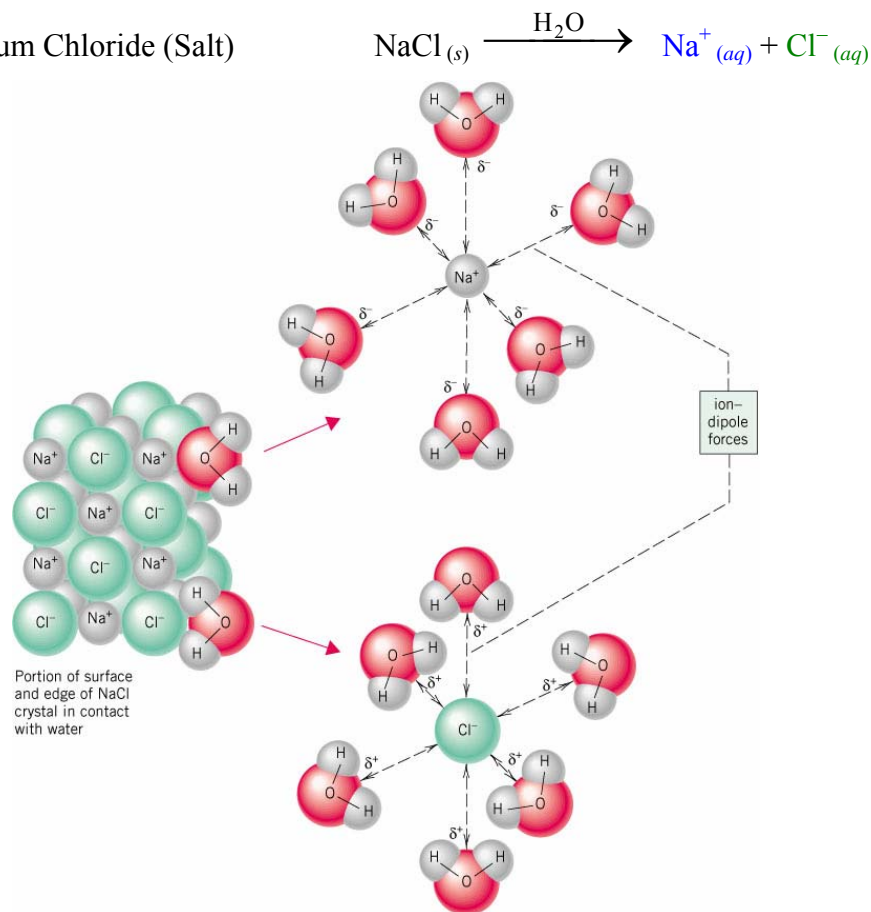
a. All hydrogen compounds in the Group (VIA) series are very polar and most have hydrogen bonds. The V-shape molecules characterized in Group (VIA) create a greater dipole moment than other series (Group (VA) with its trigonal pyramid shape and Group (VIIA) with its linear form). On the other hand, all hydrogen compounds in the Group (IVA) series are non-polar and only have London dispersion forces. Since hydrogen bonds are stronger intermolecular forces than London dispersion forces, the hydrogen compounds in the Group (IVA) series have the lowest boiling points than the counterparts in the other series.

b. NH₃, HF and H₂O have stronger hydrogen bonds than most other hydrogen compounds in their series. The difference between the electronegativities with H is the greatest in row 2 (Electronegativities increase from left to right and from bottom to top of the Table). This huge difference in electronegativities in NH₃, HF and H₂O is what causes their boiling points to buckle the trend. After NH₃, HF and H₂O the rest of the hydrogen compounds in the respective series follow the effect of London dispersion forces, the higher the molar mass, the stronger the dispersion forces, and the increase in boiling points is the result.

CH₄ in the Group (IVA) series do not buckle the trend because the entire series are non-polar. The only intermolecular force at work is the London dispersion force. Hence, CH₄ has a lower boiling point than SiH₄.

- c. **Ion-Dipole Force**: - when ionic compounds dissolve in water, the cation and anion components separate from one another. These ions are then attracted by the polar water molecules.
 - ion-dipole force is the **STRONGEST** of all intermolecular forces.

Example: Sodium Chloride (Salt)



Summary of Intermolecular Forces

- Intermolecular Bonds** involve in a compound explain its **physical properties** such as solubility (“like dissolves like”), boiling and melting points (energy involved in physical phase change).
- van der Waals Forces** consist of **London Dispersion forces** (apply to all molecules) and **Dipole Interactions** (apply to polar molecules).
- Hydrogen Bond** is the **STRONGEST** of the intermolecular bonds **amongst molecular compounds**
- Ion-Dipole Force** is the **strongest** of all **intermolecular bonds**.

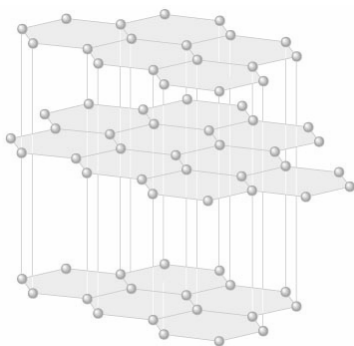
Strength of Intermolecular Forces

van der Waals Forces
 Ion-Dipole Force > Hydrogen Bond > Dipole Interaction >> London Dispersion Force
 >> (much stronger than)

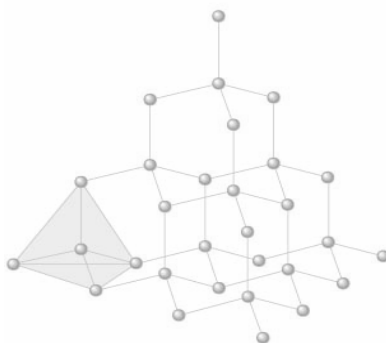
Properties of Covalent Crystalline Solids (*Metalloid Network Covalent*)

1. **Metalloids**: - consists of elements near the “staircase” of the Table (Examples are carbon in a form of diamond and silicon dioxide in a form of quartz crystal).
2. **Three-Dimensional Network Solids** as they form giant molecules by **directional covalent bonding** (contains **no discrete molecular units where an array or network of atoms are held together by conventional covalent bonds**, which are directional with dipoles of neighboring atoms).
3. **Covalent Compounds are Hard and have High Melting Points**. This is due to a more organized crystalline structure and covalent bonds are strong intramolecular bonds.
4. **Covalent Compounds are Relatively Poor Heat and Electric Conductors (or Good Heat or Electric Insulators)**. Covalent compounds do not have any charge particles like ions. Therefore, they cannot conduct heat and electricity well. *An exception is silicon elements*. (Silicon has smaller networks than diamonds, allowing some electrons to pass through. Hence, **silicon is called a semiconductor**.)

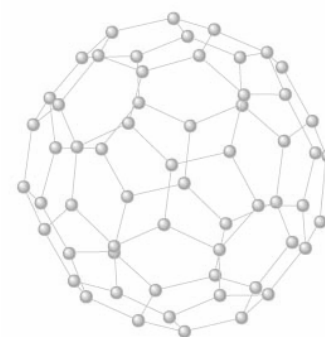
Example: Allotropes of Carbon



Carbon as *Graphite* has *weak layered with delocalized bonding network* (only some carbon atoms are connected – for each layer is $2sp^2$ hybridized which explains its hardness and brittleness). The layers are connected by weak van der Waal forces and hence, graphite can be slippery to the touch. For this reason, we can use it as a lubricant.



Carbon as *Diamond* has *strong tetrahedral network* ($2sp^3$) where all four bonding sites of each carbon atoms are connected. Hence, diamond is the hardest material known, and it has an extremely high melting point (3550°C).

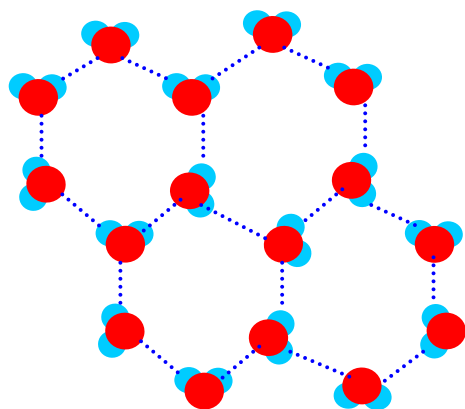


Carbon Network as C_{60} , *Buckminsterfullerene*, was discovered in 1985. *Fullerenes* are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane.

Properties of Molecular Crystalline Solids

1. **Molecular Compounds tend to have much Lower Boiling and Melting Points than ionic compounds**. This is because solid molecular compounds use **weak intermolecular forces to form their lattice structures**, which does not take much energy to break them. Their boiling points are lower than ionic compounds because there are **no ion interactions in liquid state, only intermolecular forces**.
2. **Molecular Compounds are Soft**. Again, molecular compounds **have a weak lattice structure made of intermolecular bonds** that makes them soft.

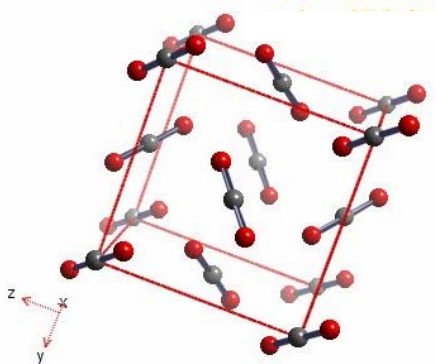
- Some Molecular Compounds and Elements tend to be More Flammable than ionic compound.** This is due to the some non-metals like sucrose and sulfur, which **combine readily with oxygen in combustion reactions**.
- Most Molecular Compounds are Insoluble in Water.** Because **water is very polar**, and it has lots of hydrogen bonds, it can only dissolve molecular compounds that are polar as well "**Like Dissolves Like**". Since **most molecular compounds are fairly non-polar**, they do not dissolve in polar water well.
- Molecular Compounds do NOT Conduct Electricity in their Solid States** due to a lack of delocalized electrons.
- Soluble Molecular Compounds do NOT Conduct Electricity in Water.** This is simply due to the fact that molecular compounds **do not dissociate into ions or electrolytes** like soluble ionic compounds do.



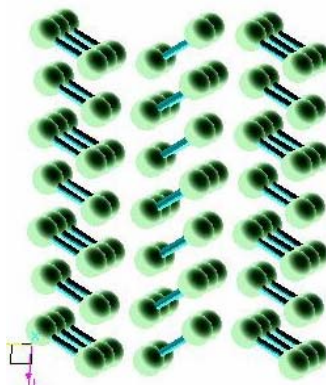
Due to the hydrogen bonds in water, it forms a *honeycomb shape* and expands in volume when it crystallizes into ice.



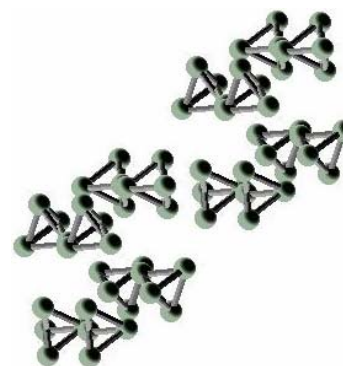
Even though no two snowflakes are alike, all of them have a basic hexagonal shape as dictated by the bent shape of water molecule and its hydrogen bonds.



Dry Ice, $\text{CO}_2(s)$, is a covalent compound that has a crystalline structure.



Even a halogen like $\text{I}_2(s)$ has a crystalline structure.



Phosphorus, $\text{P}_4(s)$ can form crystalline structure.

Assignment

12.2 pg. 418–422 #2, 3, 6 to 10, 12 to 19, 31, 32, 63, 64, 101; pg. 448 #9