

CH301 Exam Review

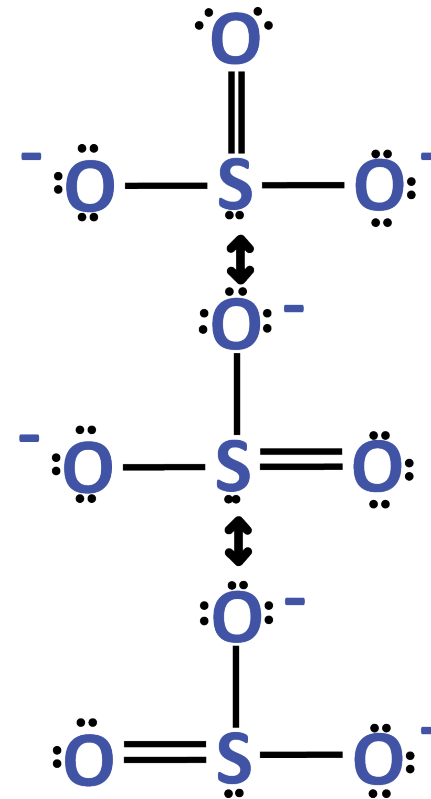
UNIT 3: BONDING AND INTERMOLECULAR FORCES

Goals for Today

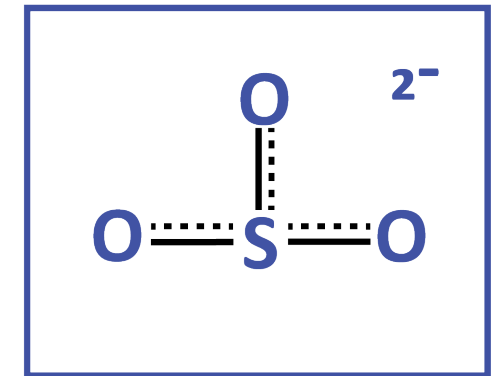
- **Unit 3 Main Topics**
 - Covalent Bonding, Lewis Structures, and Resonance
 - VSEPR Theory
 - VB Theory **Intramolecular Forces and Models (Covalent Bonding)**
 - MO Theory
 - IMF's **Intermolecular Forces and Interactions**
 - Solids

Bonding and Lewis Structures

- **Resonance:** multiple acceptable Lewis Structures are available for a given compound, meaning that the compound actually exists as the average of all acceptable structures
- **Delocalized electrons:** in the case of resonance, electrons are not confined to a single bond. Instead the electron charge is distributed over multiple bonds. We call this delocalization.
- **If you have multiple acceptable Lewis Structures in resonance, your actual structure will have the bonding character of the average. Example: Sulfite (SO_3^{2-})**



Correct Structure: three
1.33 bonds



“Acceptable” Structures: double and single bonds

Covalent Bonds and Stability

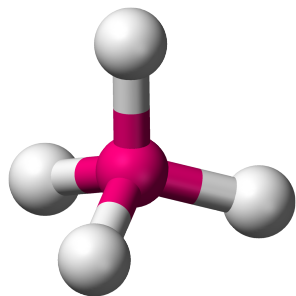
- Bond strength and bond order are important indicators of stability
- Single bonds are the weakest, lowest order, and the longest.
- Triple bonds are the strongest, highest order, and the shortest.

| Bond Type (Carbon-Oxygen) | Bond Energy (kJ/mol) | Bond Length (pm) |
|---------------------------|----------------------|------------------|
| Single | 358 | 143 |
| Double | 799 | 120 |
| Triple | 1072 | 113 |

Bonding Theories Compared

• VSEPR Theory:

- Shapes: molecular and electronic geometries
- Explains bond angles
- Focuses on the electron “regions”
- Depends on the number of electron-dense regions (bonding and lone-pair regions)



• Valence Bond Theory

- Hybrid Orbitals: sp , sp^2 , sp^3 , sp^3d , sp^3d^2
- Sigma and pi bonds
- Identifies the overlapping orbitals to “name” the bonds
- Focuses on the electron “clouds”
- Depends on the number of electron-dense regions

sp^3

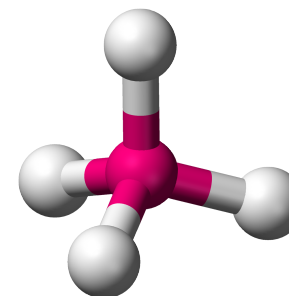
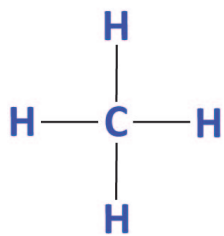
These theories might seem like a lot of information, but if you tie them together and simplify their conclusions, they actually make a lot of sense and don't require too much memorization.

• Molecular Orbital Theory

- Diagrams
- Answers three fundamental questions regarding your molecule: bond order, magnetism, HOMO-LUMO gap
- Sigma and pi bonds and **anti-bonds**
- Focuses on the electrons as “waves”
- Depends on the number of electrons

VSEPR: The one with the “Shapes”

- **Lewis Structures are a helpful way of drawing molecules. However, we use the idea of repulsions to describe the way those structures “come to life” in 3D space.**
- VSEPR gives us two different 3D geometries: **electronic geometry and molecular geometry.**
 - **Electronic geometry:** the shape of all electron-rich regions around a central atom (lone pair regions and bonding regions)
 - **Molecular geometry:** the shape of only the bonding regions around a central atom.
- VSEPR also gives us information about the bond angles. The “pure” bond angles depend on the electronic geometry. However, the “actual” bond angles require you to look at the molecular geometry and the lone pairs (lone pairs give you a slight tweak to make a smaller bond angle)



Valence Bond: The one with the “Hybrids”

- VSEPR is an accurate qualitative model, but does not properly explain the behavior of the overlapping orbitals. Valence bond explains how orbitals hybridize and overlap to form sigma and pi bonds.
- VB gives us two important conclusions: **hybridization and names of bonds**.
 - Like VSEPR, VB depends on the number of electron dense regions

Hybrids

| # of Electron-Dense Regions | Hybridization |
|-----------------------------|--------------------------------|
| 2 | sp |
| 3 | sp ² |
| 4 | sp ³ |
| 5 | sp ³ d |
| 6 | sp ³ d ² |

Valence Bond: The one with the “Hybrids”

- Naming bonds should be as simple as identifying hybridization if you can simplify the complicated Hybrid models.

Single Bonds: 1 sigma bond

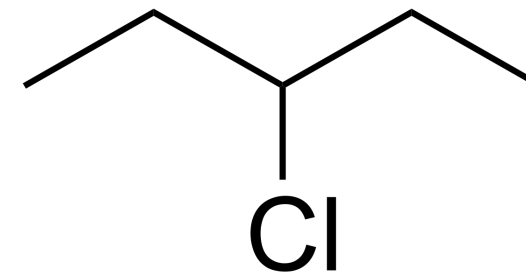
Double Bonds: 1 pi bond and 1 sigma bond

Triple Bonds: 2 pi bonds and 1 sigma bond

Sigma bonds are the **end-on-end (on axis)** overlap between hybrid orbitals (or pure 1s in the case of hydrogen because hydrogen doesn't hybridize)

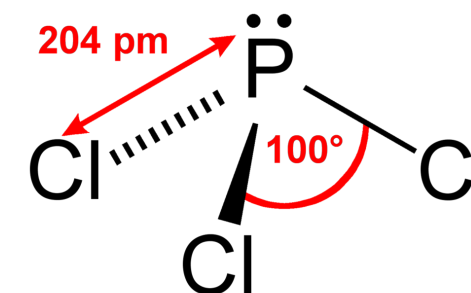
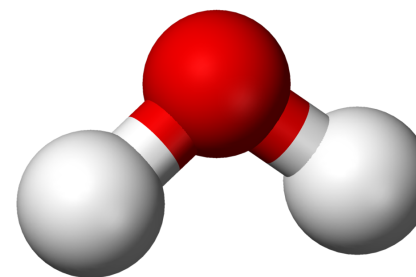
Pi bonds are the **side-by-side (off axis)** overlap between p orbitals

Determining Molecular Polarity

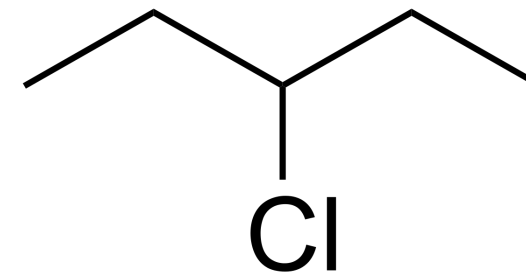


- Polarity in a molecule occurs when there is a permanent dipole moment on the molecule. This can be identified by a few rules:
 - A perfectly symmetrical molecule will always be nonpolar if its bonds are to the same atom.
 - A central atom bound to different peripheral atoms will always be polar, as long as there is at least one polar bond.
 - Lone pairs are generally an indication that the molecule is polar, except in the linear or square planar molecular geometries (where lone pairs are symmetrical).
 - Anything that hydrogen bonds is polar!

To determine the symmetry of the molecule and the presence of lone pairs, you must draw the Lewis Structures and consider the VSEPR geometry (electronic AND molecular).

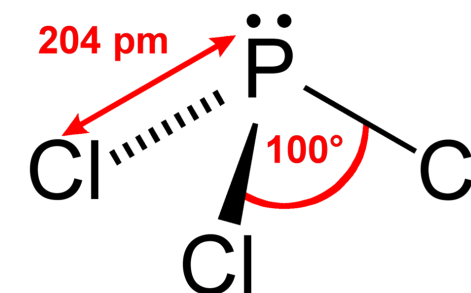
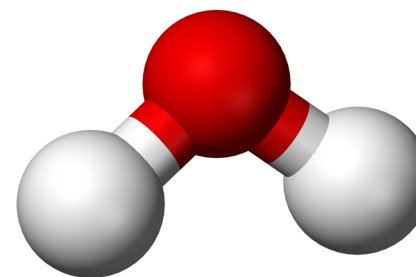


Determining Molecular Polarity



- Polarity in a **molecule** occurs when there is a permanent dipole moment on the molecule. This can be identified by a few rules:
 - A perfectly symmetrical molecule will always be nonpolar if its bonds are to the same atom.
 - Examples: CO_2 , SO_3 , SF_6 , PCl_5 , CCl_4 are non-polar molecules even though they have polar bonds
 - A central atom bound to different peripheral atoms will always be polar, as long as there is at least one polar bond.
 - Examples: CH_3Cl , CHF_3 , PCl_4F
 - Lone pairs are generally an indication that the molecule is polar, except in the linear or square planar molecular geometries (where lone pairs are symmetrical).
 - Examples: H_2O , NH_3
 - Anything that hydrogen bonds is polar!

To determine the symmetry of the molecule and the presence of lone pairs, you must draw the Lewis Structures and consider the VSEPR geometry (electronic AND molecular).

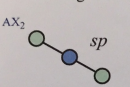
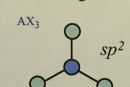
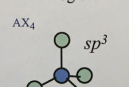
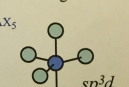



However, really all you are looking for is a net dipole moment on the molecule. Your intuition for polar molecules will increase when you practice more and more examples.

Polarity

IF X-A is a polar bond: Red is Polar Blue is nonpolar

There are only **FIVE** possible electronic geometries which you establish by counting the number of electron regions surrounding the central atom

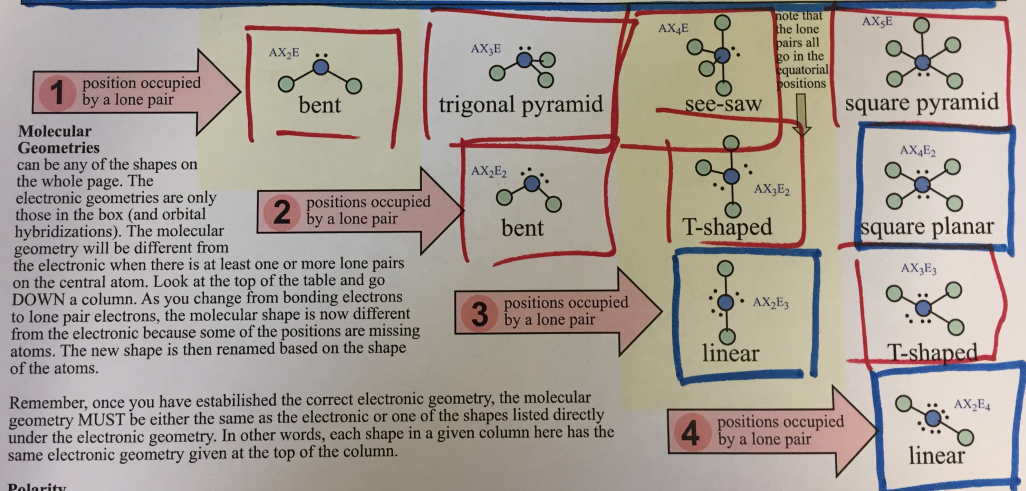
| 2 electron regions | 3 electron regions | 4 electron regions | 5 electron regions | 6 electron regions |
|--|--|--|---|---|
| AX_2  <i>sp</i> | AX_3  <i>sp²</i> | AX_4  <i>sp³</i> | AX_5  <i>sp³d</i> | AX_6  <i>sp³d²</i> |
| linear | trigonal planar | tetrahedral | trigonal bipyramid | octahedral |

1 position occupied by a lone pair

2 positions occupied by a lone pair

3 positions occupied by a lone pair

4 positions occupied by a lone pair



note that the lone pairs all go in the equatorial positions

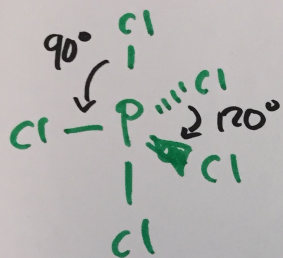
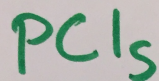
Molecular Geometries can be any of the shapes on the whole page. The electronic geometries are only those in the box (and orbital hybridizations). The molecular geometry will be different from the electronic when there is at least one or more lone pairs on the central atom. Look at the top of the table and go **DOWN** a column. As you change from bonding electrons to lone pair electrons, the molecular shape is now different from the electronic because some of the positions are missing atoms. The new shape is then renamed based on the shape of the atoms.

Remember, once you have established the correct electronic geometry, the molecular geometry **MUST** be either the same as the electronic or one of the shapes listed directly under the electronic geometry. In other words, each shape in a given column here has the same electronic geometry given at the top of the column.

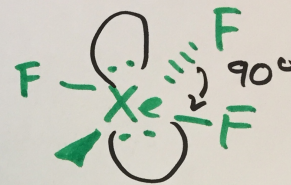
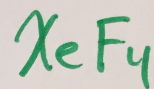
Polarity
If all the positions on the electronic geometry are the same (have the same atoms surrounding the central atom), the molecule is **NOT** polar because of the symmetry. Any of the other molecular geometries (except square planar and linear) under the box will be polar.

McCord 10/2005

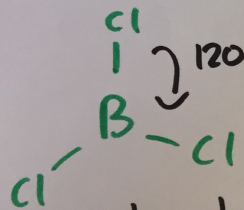
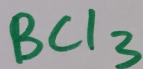
Examples



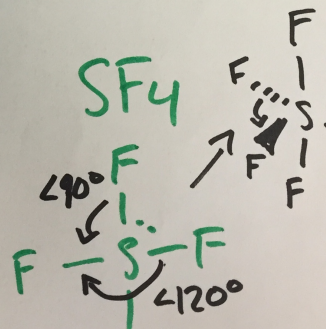
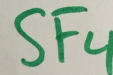
e: trig. bipyram.
 m: "
 h: sp^3d
 p? No



e: oct
 m: sq plan
 h: sp^3d^2
 p? No

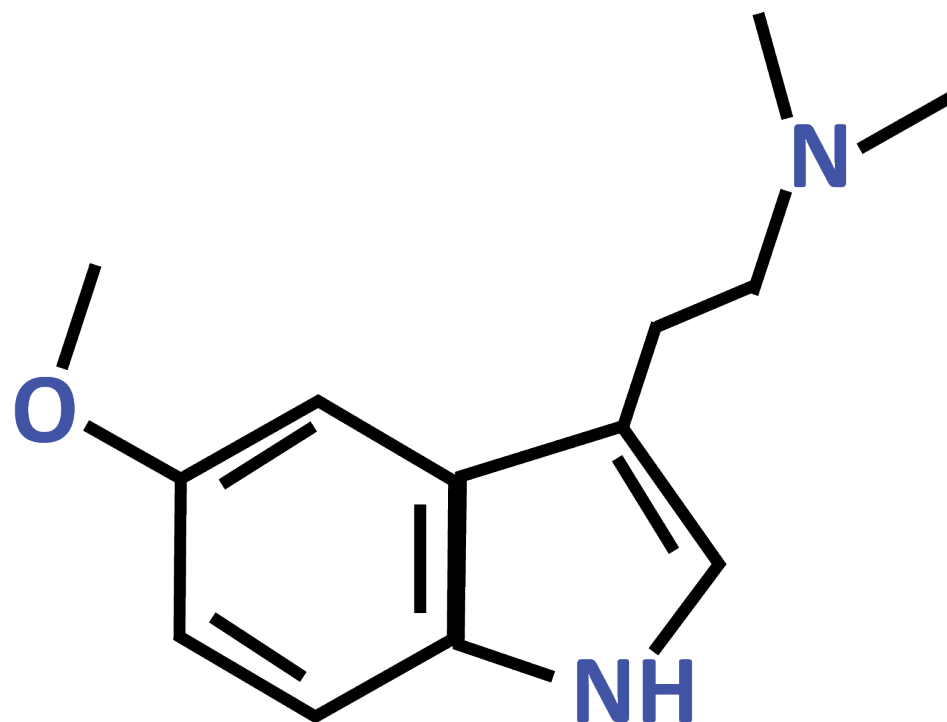


e: trig plan
 m: "
 h: sp^2 p? No

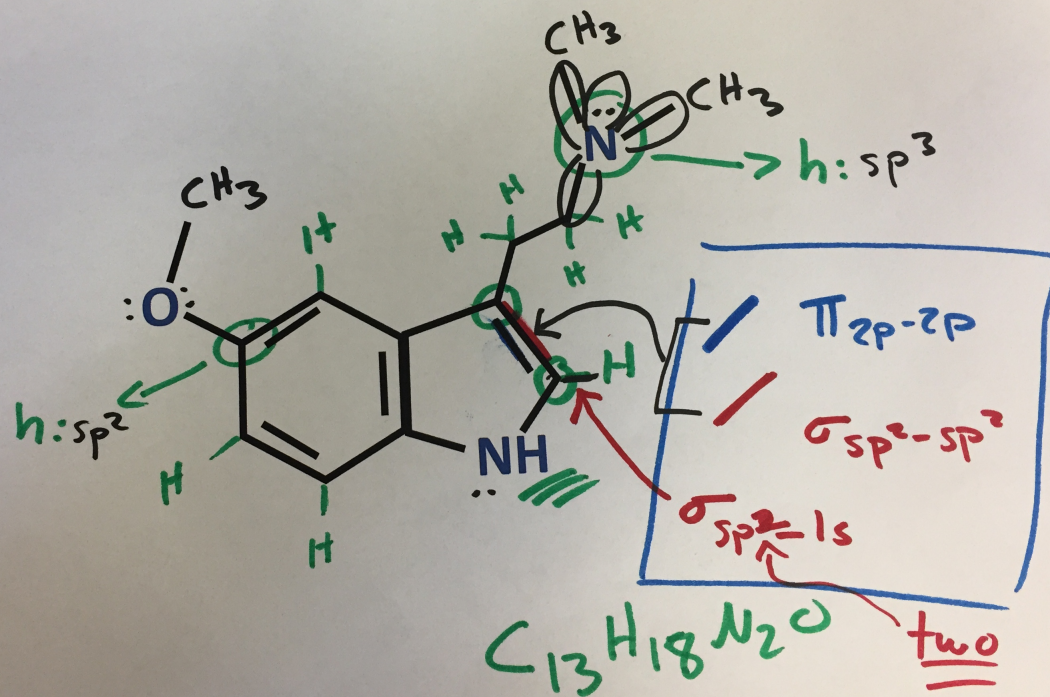


e: trig. bipyram.
 m: seesaw
 h: sp^3d p? Ya!

Organic Molecules

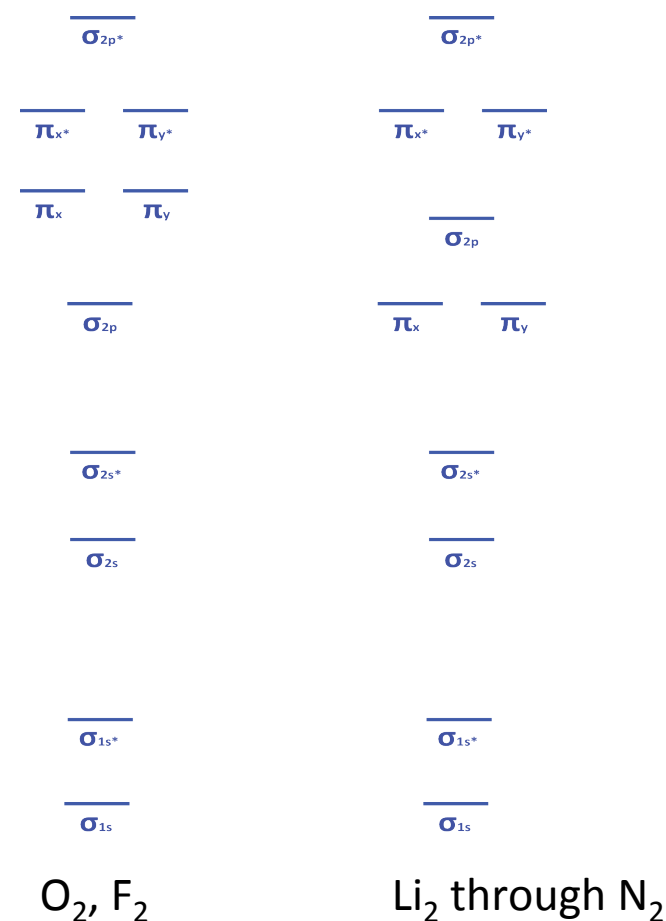


Organic Molecules



MO Theory: The one with the “Diagrams”

- **MO Theory is a quantum mechanical model for bonding that merges pure atomic orbitals into molecular orbitals**
- This theory is important because it gives us the following conclusions that VB and VSEPR cannot:
 - Stability can be described by bond order (**BO = bonding electrons – antibonding electrons**)
 - Bonding electrons aid in stability
 - Antibonding electrons lead to instability
 - Magnetism can be identified by the presence of paired or unpaired electrons in the highest occupied orbital
 - Diamagnetic: paired electrons, repelled from magnetic field
 - Paramagnetic: unpaired electrons, attracted to magnetic field
 - And of course, HOMO-LUMO...



You must memorize the diagrams to the right, their labels, and the pure atomic orbitals that go into making them.

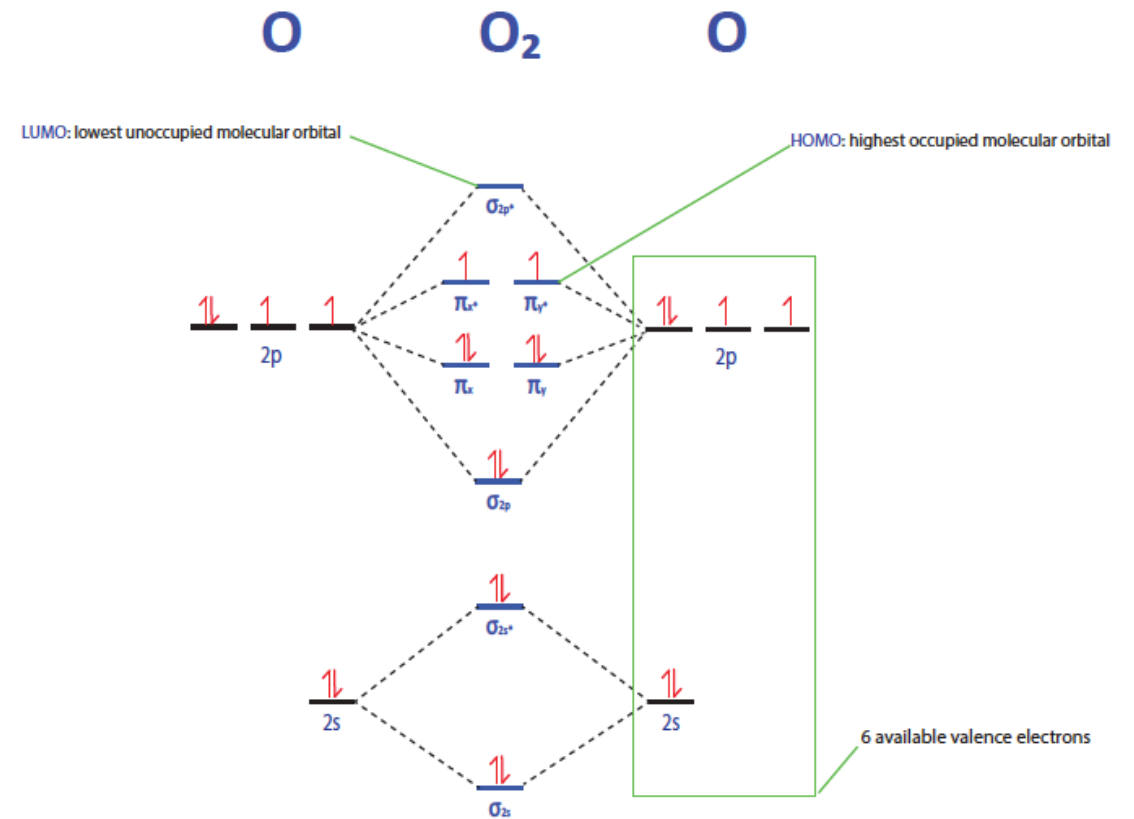
Molecular Orbital Theory: HOMO-LUMO

- One of the most important conclusions in molecular orbital theory is the energy difference between the **Highest Occupied Molecular Orbital (HOMO)** and the **Lowest Unoccupied Molecular Orbital (LUMO)**.
- This energy gap is important because it corresponds to energy of the photon emitted when an excited electron falls back down to ground state.
- Because light is important here:

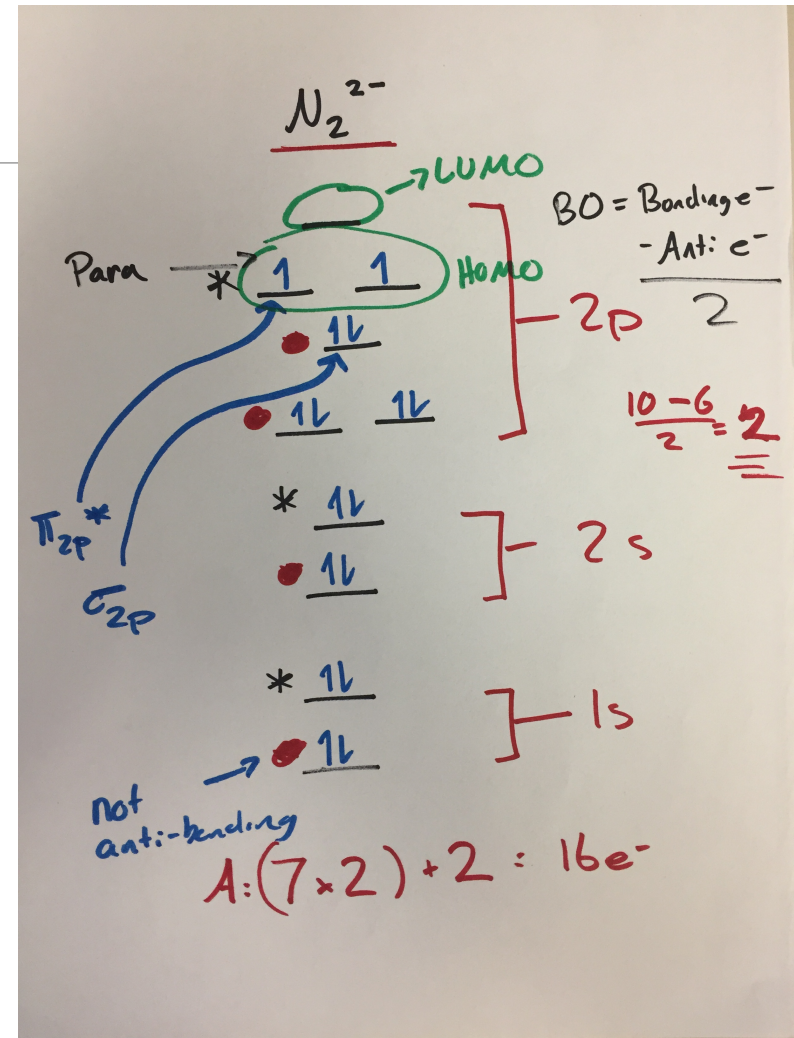
Remember:

R.O.Y.G.B.I.V.

(increasing energy, decreasing wavelength)

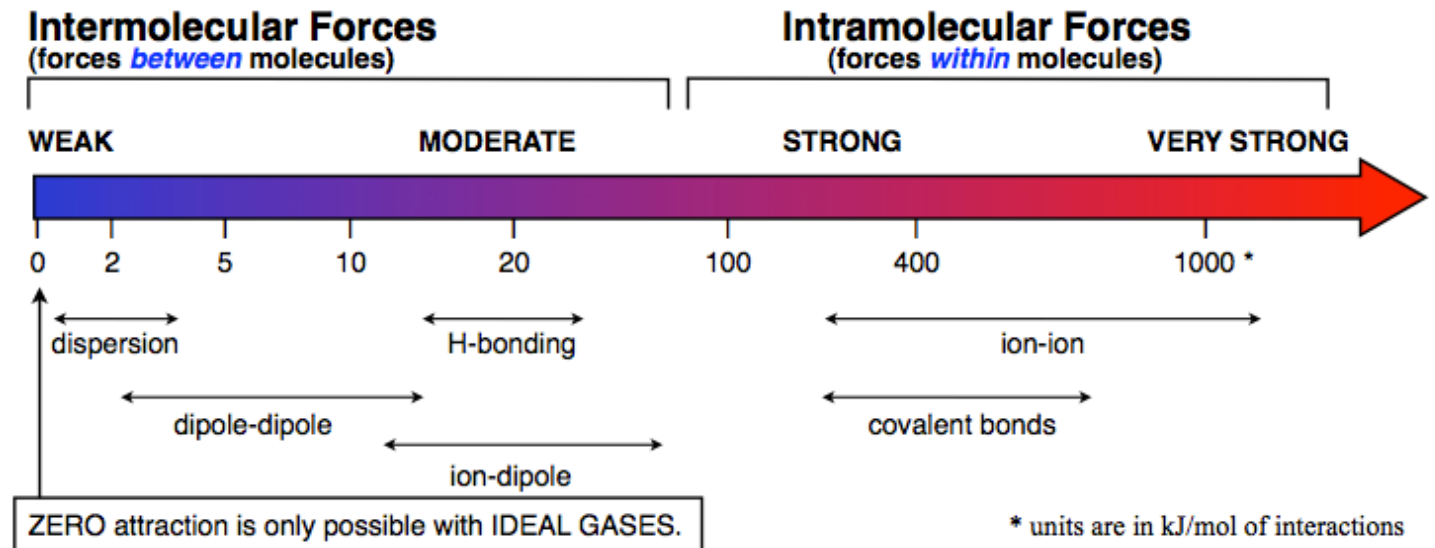


MO Diagram



Intermolecular Forces

- Intermolecular forces (IMF's) are **electrostatic** interactions between molecules.
 - IMF's vary in strength, but are weaker than **intramolecular** forces (bonds)
 - Intermolecular forces are the electrostatic "glue" that hold molecules in condensed phases
- The three types of IMF's (in decreasing strength) are:
 1. Hydrogen bonding
 2. Dipole-dipole
 3. Dispersion forces
- And they depend on:
 1. Shape
 2. Polarizability (size)
 3. **Temperature**



Dispersion Forces - Polarizability

- Dispersion forces depend on a molecule's ability to spontaneously induce a dipole. Its ability to do this is called its **polarizability** and is directly influenced by the **molecular weight** of the molecule.
 - It is often thought of as the “squishiness” or the “sloshiness” of the electron clouds
- Polarizability increases as the volume occupied by electrons increases.
 - **The larger the electron cloud, the larger the polarizability**

Gas:



Lowest Polarizability,
Lowest IMF's

Liquid:



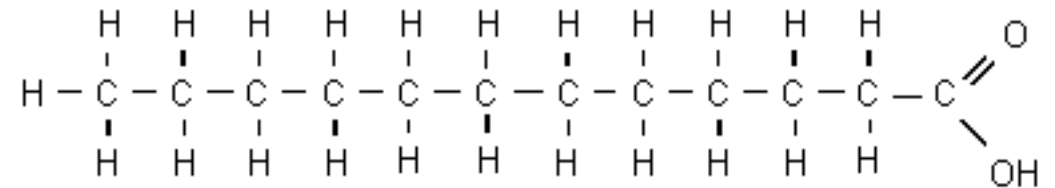
Solid:



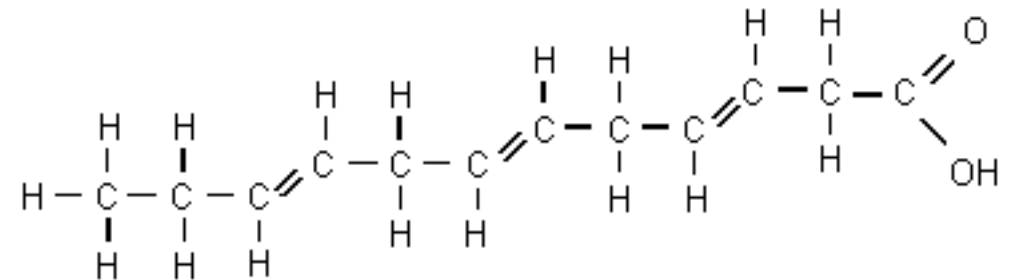
Highest Polarizability,
Highest IMF's

Dispersion Forces – Shape and “Stackability”

- The overall cumulative strength of dispersion forces increase with the number of interactions.
- **The number of interactions depends on the shape or the “stackability” of the molecule**



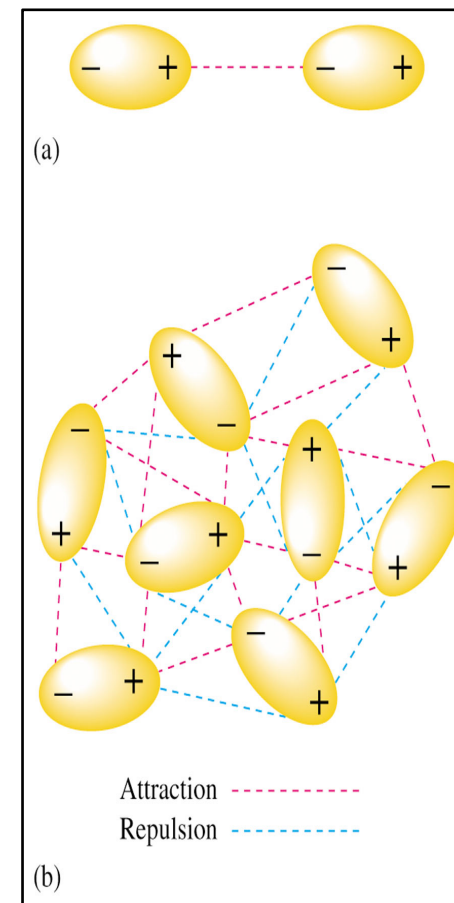
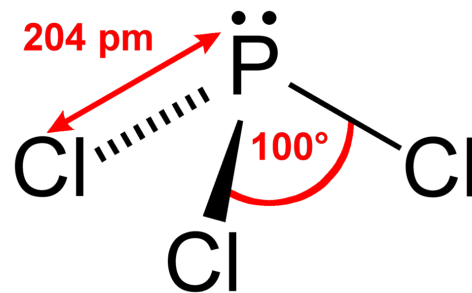
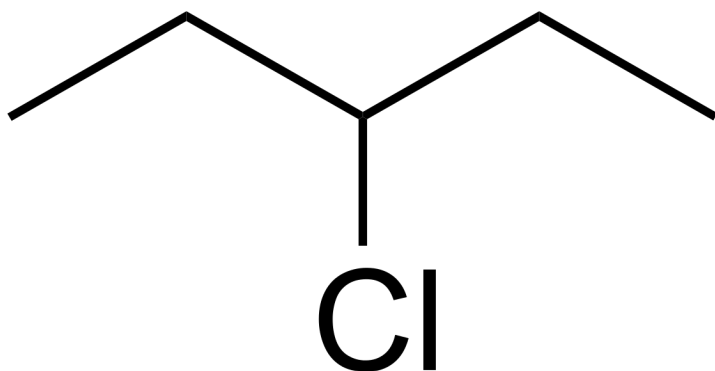
Saturated Fatty Acid



Unsaturated Fatty Acid

Dipole-Dipole Forces

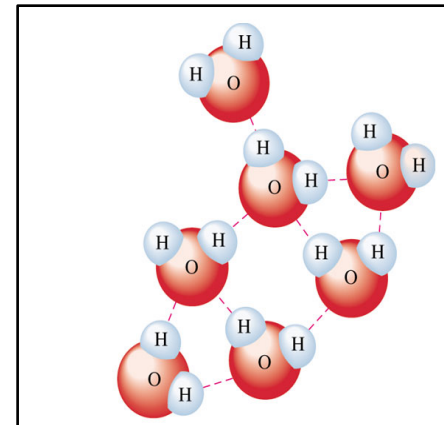
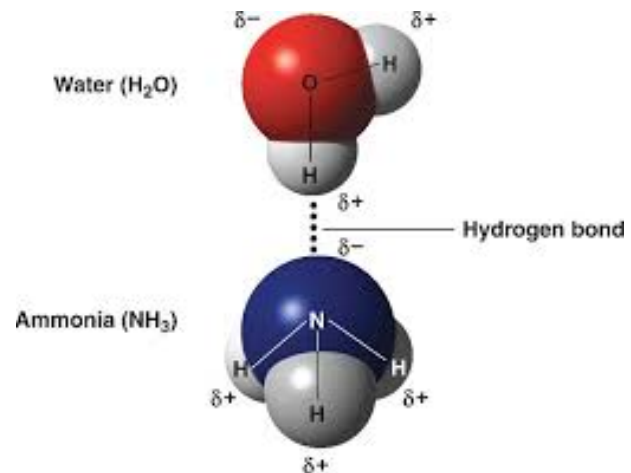
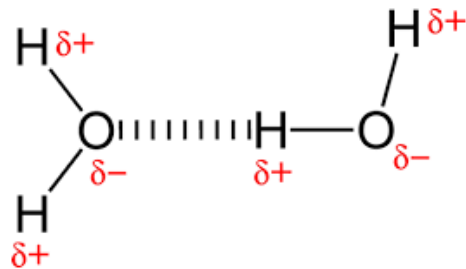
- Dipole-dipole forces require a permanently fixed dipole on a molecule.
- **Because the dipole moment is permanent, dipole-dipole forces are stronger than dispersion forces.**
- **Dipole-Dipole forces can be easily identified if you can spot out a polar molecule**



Note: the + and - in this diagram represent partial charges

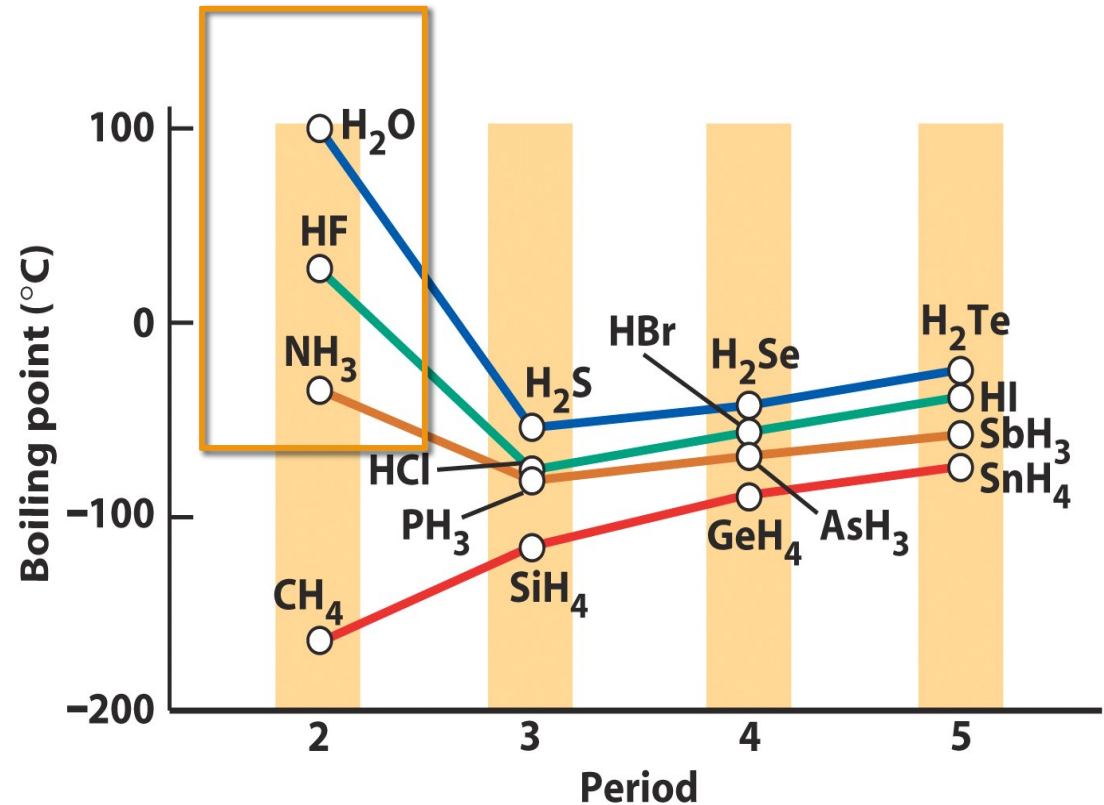
Hydrogen Bonds

- Hydrogen bonds (not actually bonds) are a particularly strong form of dipole-dipole interaction that deserve their own class of intermolecular force
- **Hydrogen bonds only occur in compounds that contain hydrogen directly bound to Nitrogen, Oxygen, and Fluorine.**



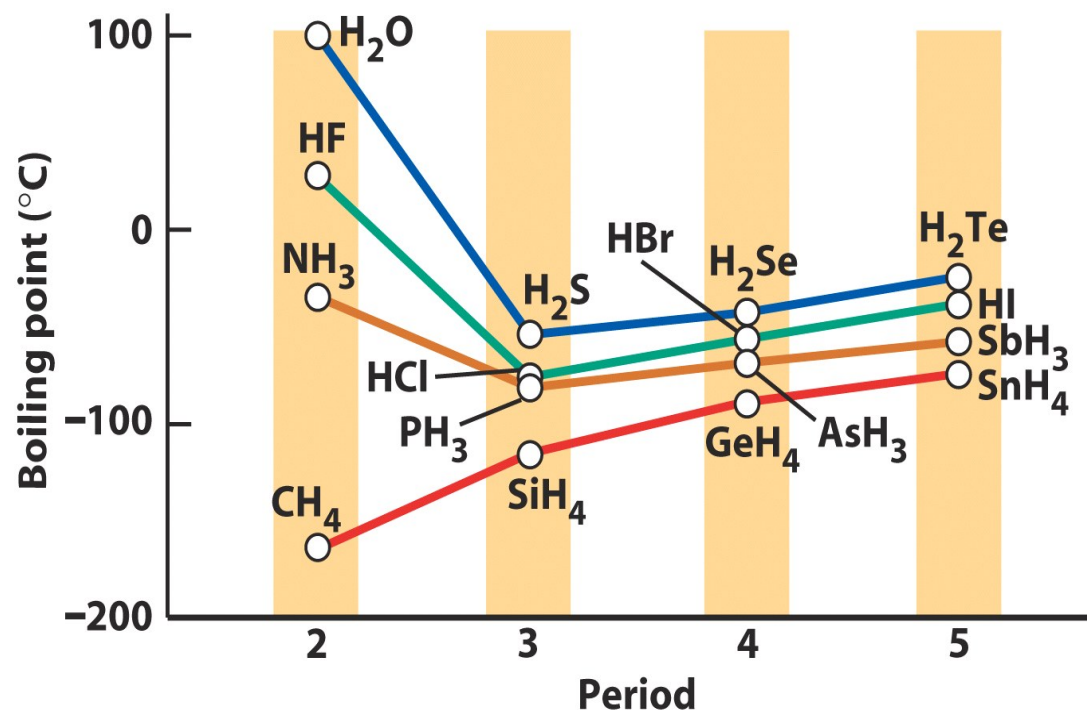
Hydrogen Bonds – Main Group Hydrides

- Hydrogen bonds explain a deviation to the trend in boiling points in the main group hydrides.
- Why is the boiling point increasing from period 3-5?
- Why doesn't this trend hold for the orange, green, and blue lines?



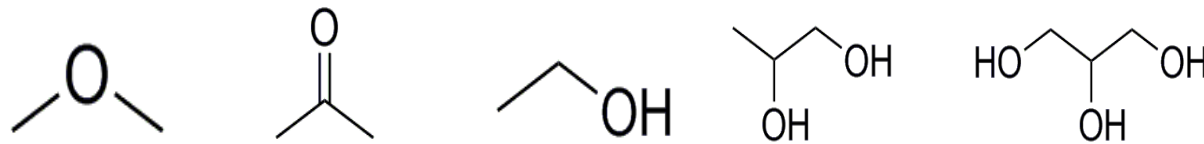
Hydrogen Bonds – Main Group Hydrides

- The key features of this graph are as follows:
 - Polarizability increases down a group
 - Shape changes across a period, leading to varying symmetries
 - Ammonia, hydrofluoric acid, and water break the trend in polarizability because they form hydrogen bonds. The red line follows the trend the best (no hydrogen bond)



Hydrogen Bonds

- The number of hydrogen bonds is important. **The more hydrogen bonds, the stronger the overall IMF's.**
- Here you can see the relationship trend in boiling point from slightly polar (dimethyl ether) to 3 H-bonds (glycerol; Propane-1,2,3 triol)

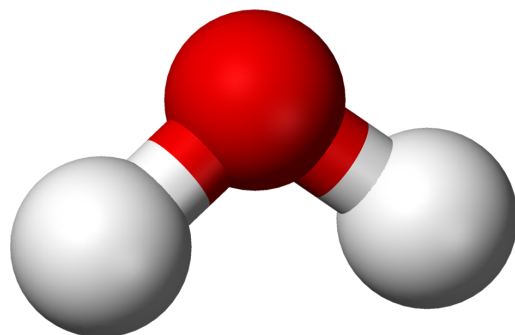


Boiling Point -24 °C 56 °C 79 °C 188 °C 554 °C

of H Bonds 0 0 1 2 3

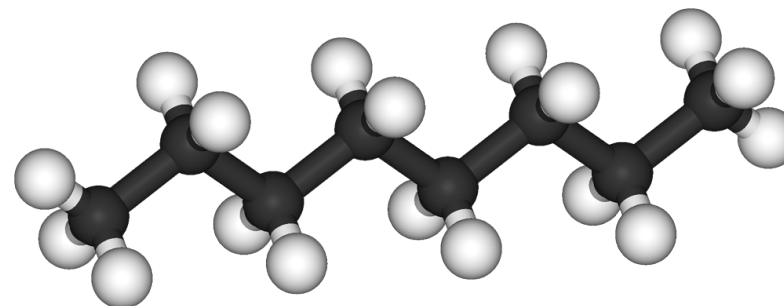
Size - Comparing IMF's

- Dispersion forces can become extremely significant with an increase in size (number of interactions)
- We can conclude that weaker intermolecular forces can become more substantial when there are more of them, resulting in overall stronger forces of attraction.
- You can't predict which of these two samples will have a higher boiling point without knowing the physical data.
 - **However, you should be able to explain why octane has a higher BP if you are given the physical data!**



BP: 100°C

Dominant IMF: Hydrogen Bonding



BP: 125°C

Dominant IMF: Dispersion

Liquid Properties Summary

Strong IMF - > High Viscosity, High BP, High Surface Tension

Weak IMF -> High Vapor pressure

High Temperature - > Lowers IMF Strength, Viscosity, and Surface Tension

High Temperature -> Raises Vapor pressure

(no effect on intrinsic properties, like boiling point, melting point, etc.)

IMF comparison

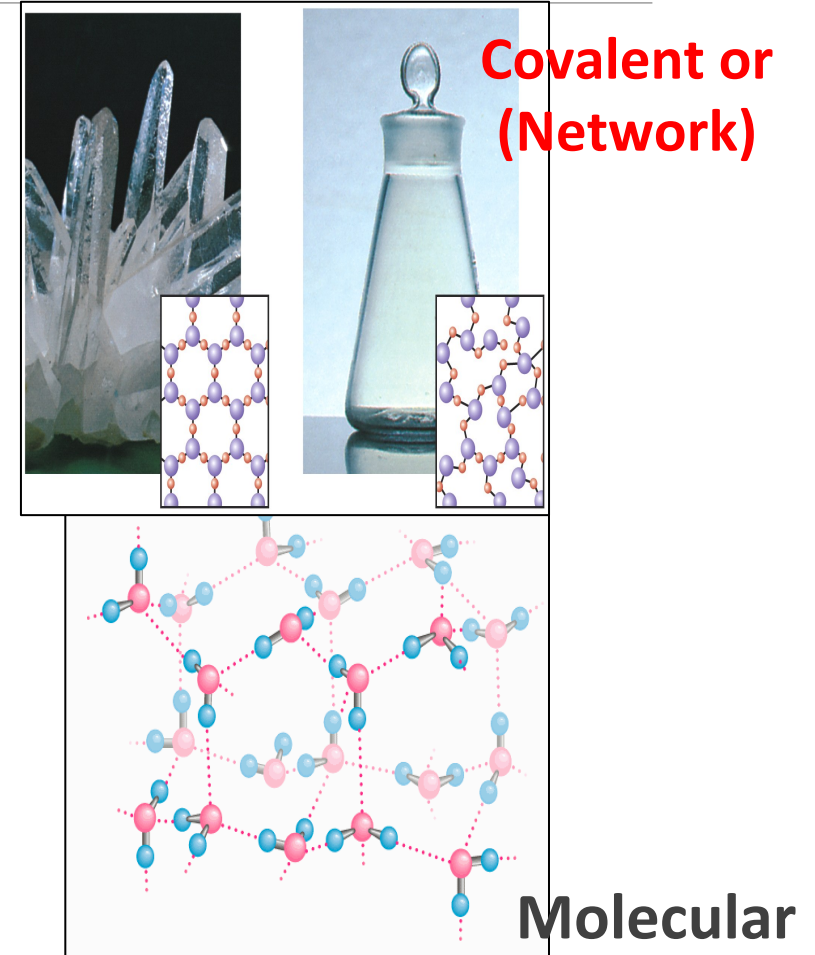
Higher BP?

GeH₄ vs. SnH₄
polarizable

SnH₄ vs. SbH₃
polar

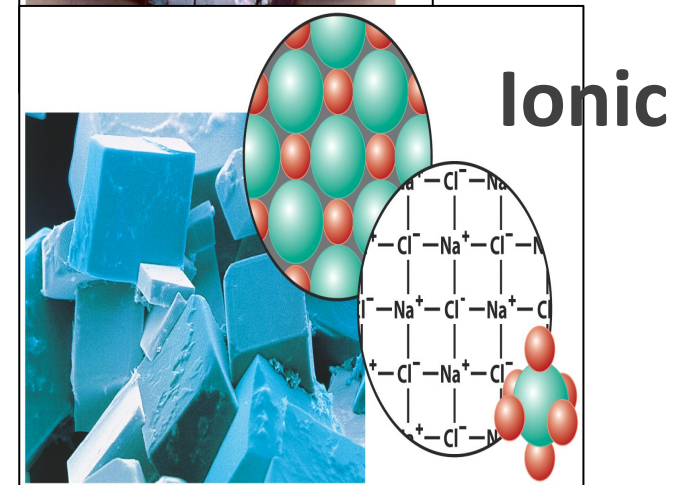
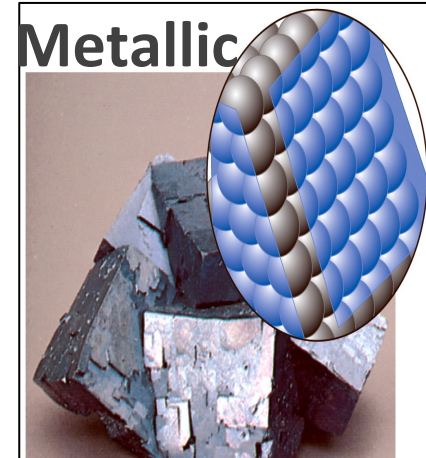
Molecular vs. Covalent Network Solids

- Molecular and Covalent Network solids are often confused because they can appear very similar on paper (CO_2 is molecular, while SiO_2 is network)
- Covalent network solids are atoms held together by **intramolecular forces** (covalent bonds in this case), resulting in extremely high (over 1000K) melting points.
- Molecular solids are molecules held together by **intermolecular forces**, resulting in low melting points (usually maxed out around 600K, but more often between 200-300K).
- **Covalent solids have small molecular weights** (think of diamond, MW = 12.01g/mol). **Molecular solids can be small or very large** (sucrose = 342 g/mol; oxytocin = 1009 g/mol)
- **Both are negligible conductors of electricity (exception: graphene contains delocalized p_z orbitals, resulting in delocalization)**



Ionic vs. Metallic Solids

- Ionic and metallic solids have similar melting points (about 1000K) and both have interactions with electricity.
- **The delocalized electrons of metallic bonds allow metallic solids to conduct electricity**
- **Ionic solids only conduct electricity when liquid or dissolved in water**
- We say that ionic solids are hard and brittle, while metallic solids are malleable and ductile.
 - This is the reason why metallic solids are used for wires and ionic solids are more like grains (think table salt)



Extra Slides

Covalent Bonds

- **Bond strength**: the energy required to break a covalent bond (also known as Bond Dissociation Enthalpy)
- **Bond order**: a measurement of the average number of chemical bonds between two atoms in a species (fractional bond order is possible in resonance and in MO theory for charged diatomics).
- **Bond length**: the distance between atoms in a bond
- **Electronegativity**: a measurement of the electron-withdrawing nature of an element in a bond. Leads to unequal sharing of electrons in a covalent bond, or polarity.
- **Resonance**: multiple acceptable Lewis Structures are available for a given compound, meaning that the compound actually exists as the average of all acceptable structures
- **Delocalized electrons**: in the case of resonance, electrons are not confined to a single bond. Instead the electron charge is distributed over multiple bonds. We call this delocalization.

Note: bond strength and order are both indicators of stability. Higher bond order means a higher bond strength, which also correlates inversely with bond length.

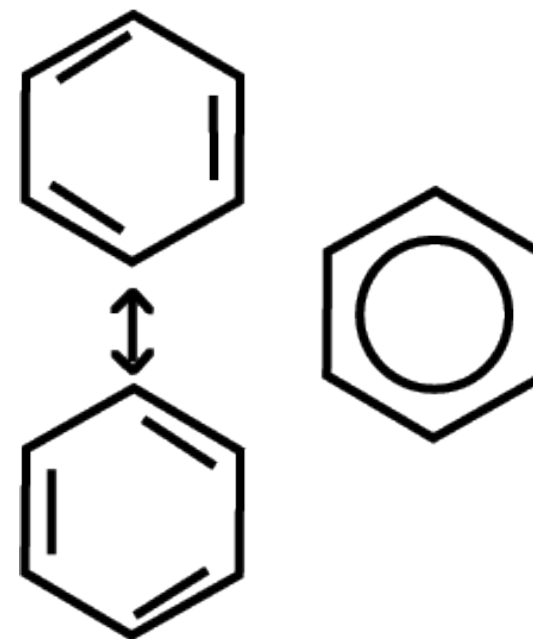
Covalent Bonds and Stability

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|------------------------------|-------------------------|---------------------|
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| Triple | 1072 | 113 |

Resonance

- Resonance occurs whenever a structure has multiple acceptable Lewis Structures.
- The science behind this is that the electrons do not exist in a single place, nor do they “flicker” back and forth between the bonds.
Instead, electrons are delocalized and their average charge is spread out over among multiple bonds



We call either the top or bottom drawings of Benzene “acceptable” structures. However, only the drawing on the right shows the actual delocalization of electrons

General Formal Charge Rules

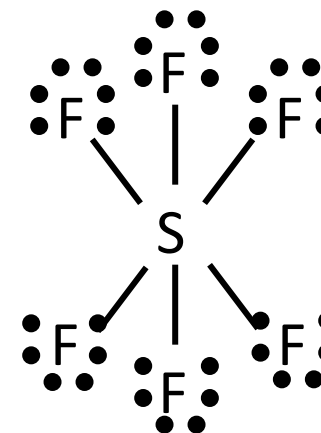
- Formal charge defines the distribution of charge throughout a molecule. More specifically, it is used to show the charge on each atom in a molecule.
- The formal charge of a molecule is the sum of the individual formal charges of the atoms in the molecule. Formal charges should be minimized in your Lewis Structures.

| Element | -1 Charge | Neutral | +1 Charge |
|----------|-----------|---------|-----------|
| Carbon | 3 bonds* | 4 bonds | 5 bonds* |
| Nitrogen | 2 bonds | 3 bonds | 4 bonds |
| Oxygen | 1 bond | 2 bonds | 3 bonds |

* In this class carbon is nearly always neutral (4 bonds). The main exception to this is Carbon monoxide.

Solving For Lewis Structure Exceptions

1. Find the number of electrons **available** (valence electrons plus the charges – subtract for positive charge, add for negative).
2. Add your bonds create the lowest possible formal charges possible.*
3. Add lone pairs to your peripheral atoms
4. If you have any electrons left based on your **available** electrons from step 1, add them to your central atom.
5. Confirm your molecule's structure by checking the formal charge

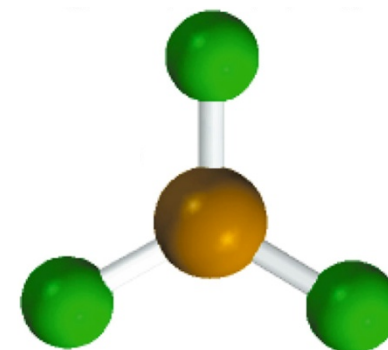
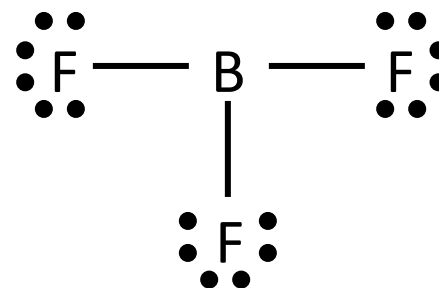
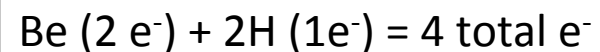
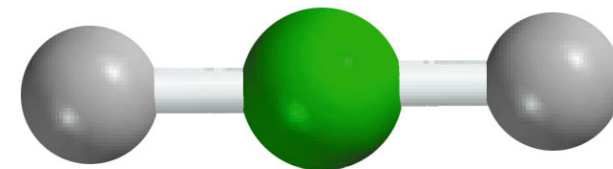


*By this I mean be smart about adding your bonds. The more you practice, the easier this step will be to make a sensible first-attempt at a structure

Incomplete Octet

- The octet rule will also be useless for central atoms with fewer than 4 valence electrons (ex: **Boron** and **Beryllium**).
- Beryllium (Be) is satisfied making **2 bonds** (4 valence e^-).
- Boron is satisfied making **3 bonds** (6 valence e^-).
- Boron and beryllium don't have many valence electrons and they have low electronegativities, so we consider them to be **electron-poor** elements with little desire to fill their octets.

Exam Tip: there are only a few good examples of the incomplete octet: BeX_2 and BX_3 , where X is either Hydrogen or a Halogen.



Incomplete Octet: Radicals

- There are a few compounds that are stable with an odd number of valence electrons
- **Radicals** are compounds with an unpaired electron in their molecular structure
- The famous of these highly reactive compounds are the nitrogen oxides (NO_x), which are heavily regulated automobile emissions
- A radical compound will always have an **odd number of available electrons**, and will not follow the $S = N - A$ rule.
- Notice how in the drawing from Nitric Oxide (right) the nitrogen has **an incomplete octet**.



Viscosity

- Boiling point can indicate if a molecule is a liquid at a given temperature, but it does not do a good job of describing of that liquid (think water versus syrup. Both are liquids, but very different).
- **Viscosity is defined as a liquid's resistance to flow.** You can think of viscous fluids as being “thick” liquids, like ketchup or syrup.
- The viscosity of a liquid is directly related to IMF's.



Strong IMF - > High Viscosity

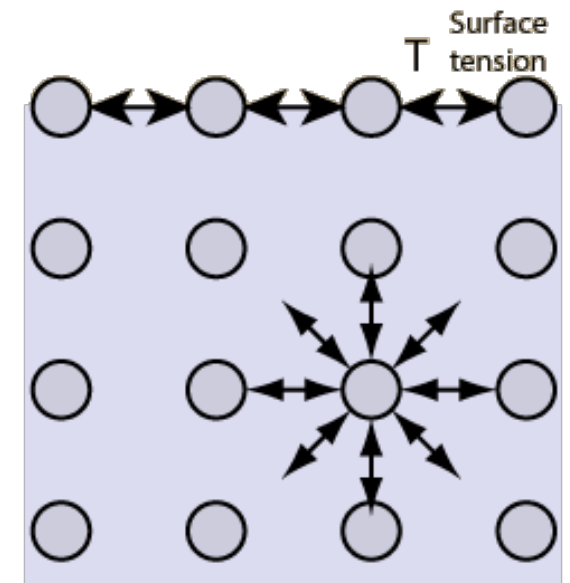
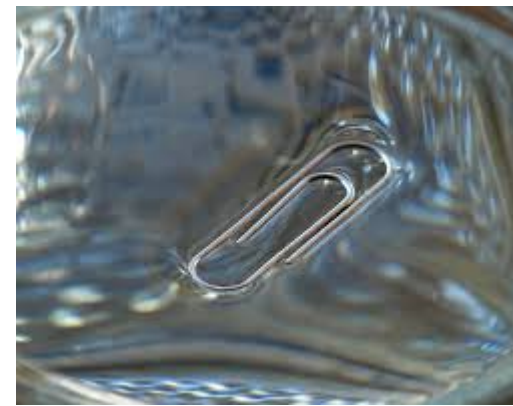
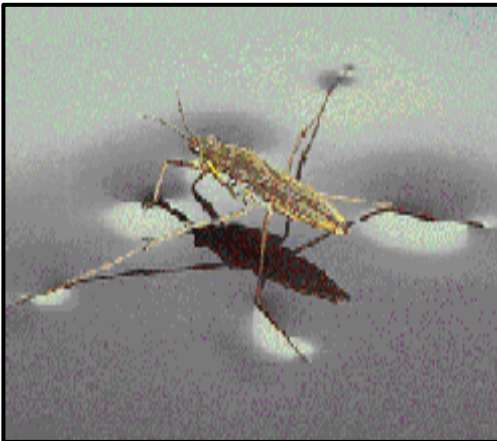
Weak IMF -> Low Viscosity

Surface Tension

- Surface Tension is the boundary formed between a liquid and another phase (either the gas above the liquid or a solid on the surface).
- **Surface tension is defined as measure of the inward forces that must be overcome in order to expand the surface area of a liquid**

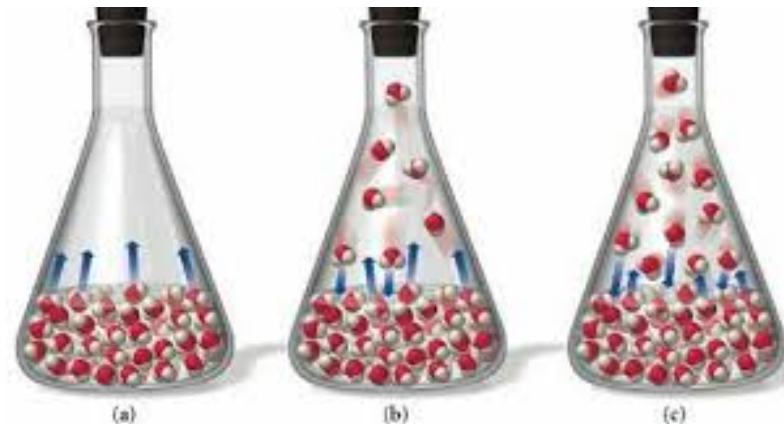
Strong IMF -> High Surface Tension

Weak IMF -> Low Surface Tension



Vapor Pressure

- For any given condensed-phase (solid or liquid) sample in a closed container, a certain amount of that sample exists in the gas phase. This is what is known as the **vapor pressure**.
- **. These molecules have enough kinetic energy to “escape” the attractions of other molecules on the surface.**
- Vapor pressure is a function of dynamic equilibrium, but more on that in CH302...



- The Vapor Pressure is a function of the IMF's of the liquid and the temperature.
 - **We are currently focused on the relationship between vapor pressure and IMFs.**

Vapor Pressure and IMF's

- If Vapor Pressure is the pressure of gas above a liquid in a closed container at a given temperature, we can easily determine that a sample with High IMF's will have a Low VP (less molecules able to overcome the IMFs and be "lifted into the gas phase).

Strong IMF -> low VP (and high boiling point)

Weak IMF -> high VP (and low boiling point)

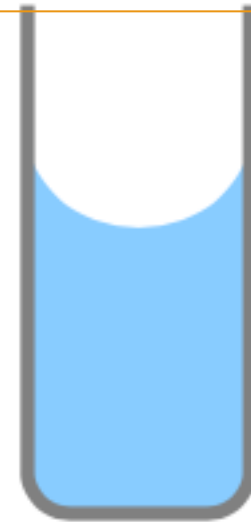
- **Therefore, while IMF's correlate directly with boiling point and viscosity, they correlate inversely with Vapor Pressure.**

Adhesion and Cohesion

- Lastly we must consider the relationship between a liquid and its container with respect to IMF's. We describe these relationships with two terms:
 1. Cohesion: the forces between a liquid and itself (think cohesion...cooperate)
 2. Adhesion: the forces between two different molecules (think adhesion..."add" another molecule). **Adhesion in this context refers to the forces between a liquid and the walls of the container.**

Two scenarios arise from these forces, depending on which one is stronger.

Adhesion Dominates



concave



convex

Cohesion Dominates

This curvature of the liquid in a container is called the meniscus

Comparing Solids

| Class | Examples | Characteristics |
|-----------|---|--|
| Ionic | NaCl, KNO ₃ , CuSO ₄ •H ₂ O | Hard, rigid, brittle; high melting/ boiling points; those soluble in water give conducting solutions |
| Network | B, C, black P, BN, SiO ₂ | Hard, rigid, brittle; very high melting points; insoluble in water |
| Metallic | <i>s</i> - and <i>d</i> - elements | Malleable, ductile, lustrous; electrically and thermally conducting |
| Molecular | BeCl ₂ , S ₈ , P ₄ , I ₂ , ice, glucose | Relatively low melting/boiling points; brittle if pure |

Comparing Solids

| Class | Electrons | Conductivity |
|--------------|------------------|--|
| Ionic | Localized | Not a good conductor (only conducts electricity in aqueous solutions or when molten) |
| Network | Localized | Not a good conductor |
| Metallic | Delocalized | Good conductor |
| Molecular | Localized | Not a good conductor |