Nuggets: Electronegativity, Bond Polarity, Lewis dot structures, Bond Order, Resonance, VSEPR, Bond angles, Molecular Polarity, Hybrid Orbitals, Intermolecular forces, Solubility/Miscibility

ELECTRONEGATIVITY: The degree to which an atom can attract electrons in a bond. The greater the electronegativity (EN), the greater the "pull" an atom has on the electron pair. (The EN value of H places it approximately between B and C on the Periodic Table.)

Trend: Increases toward F. up and to the right

TYPES OF BONDS

Nonpolar Covalent: equal sharing of e\(^-\) between two identical nonmetal elements (e.g., O\(_2\) and Cl\(_2\)).

\[ \Delta EN = 0 \] (same atoms)

Polar Covalent: unequal sharing of e\(^-\) between two nonmetals (e.g., H–F and C≡O).

\[ \Delta EN \text{ is small} \] (different atoms)

\[ \Delta EN = |EN_1 - EN_2| \] with EN\(_1\) and EN\(_2\) the EN for the 2 atoms in the bond

BOND POLARITY: as the 2 atoms get farther apart on the Periodic Table \( \Rightarrow \Delta EN \uparrow \Rightarrow \text{bond polarity} \uparrow \)

As electrons are pulled to one side of the bond a slight positive charge on one side (\(\delta^+\)) and a slight negative charge (\(\delta^-\)) on the other side of the bond with the more EN atom. The bond polarity vector points toward the more negative side of the bond (atom with greater EN):

\[ \delta^+ \rightarrow \delta^- \]

LEWIS DOT STRUCTURES

For organic molecules, connect C atoms together and make sure the #bonds is correct as remaining atoms are attached: C = 4 bonds; N = 3 bonds usually; O = 2 bonds usually; H = 1 bond

BOND ORDER (BO): Single bond \( \Rightarrow \) BO = 1; Double bond \( \Rightarrow \) BO = 2; Triple bond \( \Rightarrow \) BO = 3

Bond Order\(\uparrow\) \( \Rightarrow \) bond strength\(\uparrow\) and bond length\(\downarrow\)

\[ \text{Bond Order}_{\text{resonance}} = \frac{\text{#bonds involved in resonance}}{\text{#locations bonds involved in resonance are distributed}} \]

Resonance and Resonance Structures: In Chem 103/104 resonance structures typically have double bonds that move; common structures:

Benzene, C\(_6\)H\(_6\), BO\(_C\)–C = 1.5

Carboxylate, –CO\(_2\)^–, BO\(_C\)–O = 1.5

Amide, BO\(_C\)–O = BO\(_C\)–N = 1.5
**VSEPR - Valence Shell Electron Pair Repulsion**

1. Draw correct Lewis dot structure.
2. Determine #Domains; Domains = #lone pairs of e\(^-\) around central atom + #atoms bonded to central atom
3. Compare to table below.

<table>
<thead>
<tr>
<th>A + B = #Domains</th>
<th>#atoms bonded to central atom A</th>
<th># lone pairs on central atom B</th>
<th>Electron region geometry (ERG)</th>
<th>ERG Picture</th>
<th>Molecular geometry (MG)</th>
<th>MG Picture</th>
<th>Angles</th>
<th>Ex</th>
<th>Polarity</th>
<th>HO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>Linear</td>
<td><img src="http://en.wikipedia.org/wiki/VSEPR_theory" alt="Linear Picture" /></td>
<td>Linear</td>
<td>180(^\circ)</td>
<td>BeCl(_2)</td>
<td>NP*</td>
<td>sp</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0</td>
<td>Triangular planar</td>
<td><img src="http://en.wikipedia.org/wiki/VSEPR_theory" alt="Triangular Planar Picture" /></td>
<td>Triangular planar</td>
<td>120(^\circ)</td>
<td>BF(_3)</td>
<td>NP*</td>
<td>sp(^2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>Triangular planar</td>
<td><img src="http://en.wikipedia.org/wiki/VSEPR_theory" alt="Triangular Planar Picture" /></td>
<td>Bent</td>
<td>&lt;120(^\circ)</td>
<td>AlF(_2)</td>
<td>P</td>
<td>sp(^2)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0</td>
<td>Tetrahedral</td>
<td><img src="http://en.wikipedia.org/wiki/VSEPR_theory" alt="Tetrahedral Picture" /></td>
<td>Tetrahedral</td>
<td>109.5(^\circ)</td>
<td>CH(_4)</td>
<td>NP*</td>
<td>sp(^3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>Tetrahedral</td>
<td><img src="http://en.wikipedia.org/wiki/VSEPR_theory" alt="Tetrahedral Picture" /></td>
<td>Triangular pyramidal</td>
<td>&lt;109.5(^\circ)</td>
<td>NH(_3)</td>
<td>P</td>
<td>sp(^3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>Tetrahedral</td>
<td><img src="http://en.wikipedia.org/wiki/VSEPR_theory" alt="Tetrahedral Picture" /></td>
<td>Bent</td>
<td>&lt;109.5(^\circ)</td>
<td>H(_2)O</td>
<td>P</td>
<td>sp(^3)</td>
<td></td>
</tr>
</tbody>
</table>

P = polar molecule; NP = nonpolar molecule

* = The nonpolar (NP) molecules assume the atoms around the central atom are the same; if not, the molecule will be polar


**HYBRIDIZATION**

2 Domains \(\rightarrow\) sp hybridization
s orbital + p orbital
2 sp orbitals \(\rightarrow\) linear (180\(^\circ\))

3 Domains \(\rightarrow\) sp\(^2\) hybridization
s orbital + two p-orbitals
3 sp\(^2\) orbitals \(\rightarrow\) triangular planar (120\(^\circ\))

4 Domains \(\rightarrow\) sp\(^3\) hybridization
s orbital + three p orbitals
4 sp\(^3\) orbitals \(\rightarrow\) tetrahedral (109.5\(^\circ\))

**Sigma (\(\sigma\)) Bond:** Bond lies on the internuclear axis between the nuclei; all bonds contain a \(\sigma\) bond.

In this course \(\sigma\) bond are created from overlap of two hybrid orbitals or overlap of a 1s atomic and a hybrid orbital

\[ \sigma = HO-HO \quad (e.g., \text{sp}^2-\text{sp}^3) \quad \text{or} \quad \sigma = 1s-HO \quad (e.g., H-CH}_3\).

**Pi (\(\pi\)) Bond:** Bond does not lie on the internuclear axis and is present with double and triple bonds.

Pi (\(\pi\)) bonds are created from the overlap of 2 p-atomic orbitals

\[ \pi = p-p \]

Single bond = \(\sigma\) bond; Double bond = \(\sigma\) bond + \(\pi\) bond; Triple bond = \(\sigma\) bond + 2\(\pi\) bond
Example 1: a. Draw the Lewis dot structure for CF₂=CH₂. b. Identify the hybridization for each atom. c. Identify what orbitals make up each bond.

Answer 1:

INTERMOLECULAR FORCES (IMF): Forces between molecules, not within a molecule.
- **H-bonding:** Criteria: \( H \) bonded to \( N, O, \) or \( F \); look for \(-OH\) groups; examples: \( \text{CH}_3\text{OH}(l) \) (alcohols); \( \text{H}_2\text{O}(l) \); \( \text{CH}_3\text{COOH}(l) \) (carboxylic acids); \( \text{CH}_3\text{NH}_2 \) (amines); H-bonding IMF are usually stronger than Dipole-Dipole and London Dispersion Forces.

\[
\begin{align*}
\text{H} & \rightleftharpoons \text{H} \\
\text{O} & \rightleftharpoons \text{O} \\
\text{H} & \rightleftharpoons \text{H}
\end{align*}
\]

- **Dipole–Dipole:** Criteria: polar molecule; example: \( \text{F} \rightarrow \text{Cl} \)

**Polar molecules:**
- diatomic \( \text{X–Y} \)
- compounds with a carbonyl group: \( \text{C} \rightarrow \text{O} \)

- chemicals with \( \text{O} \), \( \text{N} \), and \( \text{S} \), and
- VSEPR Table: 2\( |0, 3\)|0, 4\( |0 \) with different atoms around central atom
- VSEPR Table: 2\( |1, \) 3\( |1, \) 2\( |2 \) always polar

**Nonpolar molecules:**
- diatomic \( \text{X–X} \)
- hydrocarbons (only \( \text{H} \) and \( \text{C} \); \( \text{C}_x\text{H}_y \))
- VSEPR Table: 2\( |0, 3\)|0, 4\( |0 \) with same atoms around central atom

- **London Dispersion Forces (LDF)** = Induced Dipole = Instantaneous Dipole: Criteria: has electrons; occurs in all molecules and individual atoms; caused by electrons shifting to one side of the molecule/atom creating an instantaneous dipole within the molecule; hydrocarbons have only LDFs for IMFs

\[ \#e^- \uparrow \Rightarrow \text{LDFs} \uparrow \]

DETERMINE WHICH MOLECULE HAS LARGEST IMFs
Determine IMF and compare: IMFs \( \uparrow \) (generally) \( \Rightarrow \) \text{H-Bonding} > Dipole–Dipole > LDF
If two molecules have the same IMF:
- **H-bonding:**
  1. more \(-\text{OH} \) or \(-\text{NH} \) groups \( \Rightarrow \) more H-bonding \( \Rightarrow \) larger IMFs
- **Dipole-dipole:**
  1. one molecule is more polar when \( \Delta\text{EN} \) is greater \( \Rightarrow \) greater permanent dipole \( \Rightarrow \) larger IMFs
  2. geometric isomers: cis-isomer: polar; trans-isomer: nonpolar (see HelpSheet #3)
- **LDFs only:**
  1. larger molecule \( \Rightarrow \) more electrons \( \Rightarrow \) greater LDFs \( \Rightarrow \) larger IMFs
  2. hydrocarbon molecules: linear molecule > branched molecule \( \Rightarrow \) greater LDFs \( \Rightarrow \) larger IMFs

IMFs \( \uparrow \) \( \Rightarrow \) Boiling Point \( \uparrow \)
SOLUBILITY: Liquids dissolving into liquids = miscibility

In general: Like likes Like
- polar substances dissolve into polar substances (dissolve = miscible);
- nonpolar substances (e.g., hydrocarbons!) dissolve into nonpolar substances (dissolve = miscible);
- polar and nonpolar substances don’t dissolve into one another (don’t dissolve = immiscible)
- more H-bonding regions ⇒ more polar ⇒ more soluble in water

1. Answer the questions below about the structure and bonding in this molecule. (Hint: Draw in the lone pair e−.)
   a. What is the angle between the H-C-O labeled with an “a”?
   b. What is the electron region geometry around the carbon atom labeled “b”?
   c. What is the molecular geometry around the oxygen atom labeled “c”?
   d. What is the hybridization of the carbon atom labeled “a”?
   e. What orbitals overlap to make the bond between the carbon atom labeled “d” and the attached hydrogen atom?
   f. What orbitals overlap to make the pi (π) bond between the carbon atom labeled “a” and the oxygen atom attached to it?
   g. What is the electron region geometry around the carbon atom labeled “d”?
   h. How many lone pairs of electrons are there in the molecule?

2. Answer the following questions for the molecule to the right.
   a. Draw in the lone pairs of electrons in the structure.
   b. What is the bond order for the bond labeled “a”?
   c. What is the hybridization on the S labeled “b”?
   d. What is the angle for the C–O–H on the O labeled “c”?
   e. What orbitals are used to form the bond labeled “e”?
   f. How many σ and π bonds are in the molecule?
   g. What is the electron region geometry around the S atom labeled “b”?
   h. What orbitals are used to form the bonds labeled “a”?

3. For each set of chemicals, order them from lowest to highest boiling point.
   I. CH₄, C₃H₈, C₂H₆  II. CH₃CH₂Br, CH₃CH₂F, CH₃CH₂Cl  III. H₂O, CH₃OH, CH₃OCH₃

4. Place the molecules in order of most to least soluble in water.
   CH₃CH₂CH₂OH, CH₃CH₂CH₂CH₂CH₂CH₃, HOCH₂CH₂OH

5. What is the electron regional geometry, hybridization, and angle around the bold underlined C atom of each molecule below? (Hint: Draw the Lewis dot structure for each molecule.)
   a. CH₄  b. CH₃CH₃  c. CH₂CH₂  d. HHC=CH

6. Draw Lewis dot structures for each of the following molecules. Organic structures will have the following bonding: C = 4 bonds (always for this class); N = 3 bonds; O = 2 bonds
   a. C₂H₆  b. C₂H₄  c. CH₃CH₂OH  d. CH₃CH₂OCH₂CH₃
   e. C₆H₆ (benzene = 6-membered carbon ring; see page 1 of this HelpSheet for a structure)
7. I. Which molecule below has the strongest C—O bond?  
(Hint: Draw the Lewis dot structure and determine BO)
II. Which molecule below has the longest C—O bond?
  
a. CO$_3^{2-}$  
b. CH$_3$CH$_2$OH  
c. CO  
d. H$_2$CO (C is central atom)  
e. Same strength/length.

**ANSWERS**
1. a. 120°  
   {3 domains ⇒ triangular planar ⇒ 120°}
   b. tetrahedral  
   {4 domains ⇒ tetrahedral}
   c. bent  
   {4 domains ⇒ 2 atoms + 2 lone pairs ⇒ MG = bent}
   d. sp$^2$  
   {3 domains ⇒ sp$^2$}
   e. σ: 1s(H)–sp$^2$(C)  
   {single bond ⇒ σ bond; σ bonds made from HO–HO or HO-1s}
   usually; C has 3 domains ⇒ sp$^2$; σ bond = 1s(H)–sp$^2$(C)
   f. π: p(C)–p(O)  
   {all π bonds made from overlap of p-orbitals; π bond = p(C)–p(O)}
   g. triangular planar  
   {C atoms has 3 domains ⇒ triangular planar}
   h. 6  
   {see diagram}

2. a.  
   b. 2  
   {double bond with no resonance ⇒ bond order = 2}
   c. sp$^3$  
   {4 domains around S ⇒ sp$^3$}
   d. <109.5°  
   {around the vertex atom (O atom) there are 3 domains ⇒ tetrahedral ⇒ 109.5°}
   e. 1s(H)–sp$^3$(N)  
   {single bond ⇒ σ bond; σ bonds made from HO–HO or HO-1s}
   usually; N has 4 domains ⇒ sp$^3$;  
   σ bond = 1s(H)–sp$^3$(N)
   f. 22σ , 2π  
   {single bond = σ bond; double bond = σ + π bond; triple bond = σ + 2π bonds}
   g. tetrahedral  
   {4 domains around S ⇒ tetrahedral ERG}
   h. π: p(C)–p(C); σ: sp$^2$(C)–sp$^2$(C)  
   {double bond = σ + π bond; σ bonds made from HO–HO or HO-1s}
   usually; each C has 3 domains ⇒ sp$^2$; σ bond = sp$^2$(C)–sp$^2$(C); all π bonds made from overlap of p-orbitals; p bond = p(C)–p(C)

3. I. CH$_4$ < C$_2$H$_6$ < C$_3$H$_8$  
   {as #e$^-$ ↑ ⇒ LDF↑ ⇒ IMF↑ ⇒ boiling points↑}
   II. CH$_3$CH$_2$F < CH$_3$CH$_2$Cl < CH$_3$CH$_2$Br  
   {as #e$^-$ ↑ ⇒ LDF↑ ⇒ IMF↑ ⇒ boiling points↑}
   III. CH$_3$OCH$_3$ < CH$_3$OH < H$_2$O  
   {IMFs↑ ⇒ Boiling Point↑; CH$_3$O–CH$_3$ has dipole-dipole IMFs; CH$_3$O–H has H-bonding; H$_2$O also has H-bonding but has 2 H atoms that can H-bond; H–O–H so it has greater H-bonding while CH$_3$OH only has 1 H that can undergo H-bonding; CH$_3$OCH$_3$ has no H-bonding, is polar and therefore has dipole-dipole IMFs which are usually weaker than H-bonding and therefore has the lowest bp; CH$_3$OH is next because it has H-bonding but less H-bonding than H$_2$O; CH$_3$OCH$_3$ < CH$_3$OH < H$_2$O}
4. most soluble to least soluble in water: \( \text{HOCH}_2\text{CH}_2\text{OH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)

{Water is polar and substances that are polar will be soluble (miscible) in water. Both \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \) and \( \text{HOCH}_2\text{CH}_2\text{OH} \) are polar because of the polar \(-\text{OH}\) groups. Since chemical \( \text{HOCH}_2\text{CH}_2\text{OH} \) has two \(-\text{OH}\) groups it has more polar regions than \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \) with only one \(-\text{OH}\) group. The substance with more polar regions will be more soluble in another polar substance such as water. Chemical \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \) is a hydrocarbon and is therefore nonpolar and least soluble in water.}

5. a. tetrahedral, \( \text{sp}^3 \) {from LDS: \( \text{C has 4 domains} \Rightarrow \text{tetrahedral, sp}^3, 109.5^\circ \)}

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

b. tetrahedral, \( \text{sp}^3 \) {from LDS: \( \text{C has 4 domains} \Rightarrow \text{tetrahedral, sp}^3, 109.5^\circ \)}

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

c. triangular planar, \( \text{sp}^2 \) {from LDS: \( \text{C has 3 domains} \Rightarrow \text{triangular planar, sp}^2, 120^\circ \)}

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

d. linear, \( \text{sp} \) {from LDS: \( \text{H} \text{--C--C--H} \text{ C has 2 domains} \Rightarrow \text{linear, sp, 180}^\circ \)}

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

6. a. 

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

b. 

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

c. 

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

d. 

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

e. 

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

7. I. c \{as \( \text{BO} \uparrow \Rightarrow \text{bond strength} \uparrow; \text{BO} = 3 \) for structure c\}

\[
\begin{pmatrix}
\cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot \\
\end{pmatrix}
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C}
\end{array}
\]

a. \( \text{BO} = 4/3 \); b. \( \text{BO} = 1 \); c. \( \text{c} \equiv \cdot \); d. \( \text{H} \); BO = 2

II. b \{as \( \text{BO} \uparrow \Rightarrow \text{bond length} \downarrow; \text{BO} = 1 \) for structure b\}