Outline

- Discuss General Class Information (Professor Imperiali)
- General Introduction to Organic Chemistry

I. Review of Lewis Bonding Theory (Read Chapter 1)
   A. Ionic Bonding (1-3A, 6, 8)
   B. Covalent Bonding (1-3B, 4)
      1. Multiple Bonding (1-5)
      2. Formal Charge (1-7)
   C. Short-Hand for Chemists
      1. Line-Angle Formulas: Simplified Structures (1-10)
      2. Dashes and Wedges: Molecules in 3-D (2-5)
      3. Curved Arrow Formalism: Electrons in Motion (1-14)

II. Resonance (1-9)
   A. Rules for Drawing Resonance Structures
   B. Relative Energy of Resonance Structures
   C. Structure and Reactivity from Resonance

Suggested Problems: 1-25, 36, 39, 41

Problem Set #1 Posted: Due Monday 2/10 by 4pm
Organic Chemistry: What is it?

1780: Organic compounds very complex and only obtained from living sources (vitalism)

Vitalism: Belief that a "magic" vital force, present in plants and animals, is necessary for the synthesis of organic compounds

1789: Antoine Laurent Lavoisier observed that organic compounds are composed primarily of carbon and hydrogen

1828: Friedrich Wohler synthesized an organic compound (urea) from inorganic compounds (lead cyanate and ammonium hydroxide).

\[
\begin{align*}
\text{Pb}^+\text{NCO}^- & \quad \text{NH}_4^+\text{OH}^- & \quad \text{NH}_4^+\text{NCO}^- \\
\text{lead cyanate} & \quad \text{ammonium hydroxide} & \quad \text{ammonium cyanate} \\
\text{inorganic} & \quad \text{heat} & \quad \text{urea} \\
\end{align*}
\]

Modern organic chemistry is the chemistry of carbon compounds.

"The Age of Organic Chemistry"

• > 95% of All Known Compounds Composed of Carbon

• Organic Chemistry Crucial to Our Way of Life: Clothing, Materials (Polymers), Petroleum, Medicine, OUR BODIES

• > 50% of Chemists Are Organic

**STRUCTURE**

Determining the Way in Which Atoms Are Put Together in Space to Form Complex Molecules

**MECHANISM**

Understanding the Reactivity of Molecules: How and Why Chemical Reactions Take Place

**SYNTHESIS**

Building Complex Molecules From Simple Molecules Using Chemical Reactions
Why Carbon?

- Carbon forms a variety of strong covalent bonds to itself and other atoms.
- This allows organic compounds to be structurally diverse.

Why Does Carbon Bond in This Way?

I. Review of Lewis Bonding Theory (READ CH 1)

- Atoms transfer or share electrons to gain a filled valence shell of electrons.

A. Ionic Bonding

- Between atoms of widely different electronegativity (ΔEN>2); usually a metal and a non-metal; atoms held together by electrostatic attraction, not electron sharing

  e.g. LiF is ionic (EN: Li = 1.0, F = 4.0)

\[
\begin{align*}
\text{Li} &\rightarrow \text{Li}^+ + e^- & \Delta H = +123.6 \text{ kcal/mol} \\
& 1s^22s^1 & 1s^2 = [\text{He}] \\
\text{F} & + e^- \rightarrow F^- & \Delta H = -78.3 \text{ kcal/mol} \\
& 1s^22s^22p^6 & 1s^22s^22p^6 = [\text{Ne}]
\end{align*}
\]

- Using Lewis Dot Structures:

\[
\begin{align*}
\text{Li} + \cdot \cdot \cdot F : \cdot \cdot \cdot &\xrightarrow{\text{electron transfer}} \text{Li}^{\cdot\cdot\cdot} + F^{\cdot\cdot\cdot} & \text{LiF} \text{ (ionic bond)} \\
& \text{Bond Energy } \sim 138 \text{ kcal/mol}
\end{align*}
\]
B. Covalent Bonding (Electron Sharing)

- Very important in organic molecules!
- Between atoms of similar electronegativity; usually non-metallic

**e.g.** COCl₄ is covalent . . . Why?

- Large thermodynamic penalty for ionization of carbon to C⁴⁺

\[
\begin{align*}
\text{C} & \quad \xrightarrow{\text{X}} \quad \text{C}^4^+ & + & 4e^- & \quad \Delta H = +1480.7 \text{ kcal/mol} \\
1s^22s^22p_x^12p_y^1 & \quad 1s^2 = [\text{He}] \\
\end{align*}
\]

- Instead, each chlorine atom shares one valence electron with carbon so that every atom has a filled octet.

\[ \text{Kekule Drawing} \]

- Each chlorine atom still has three unshared pairs of electrons (lone pairs).

**lone pair:** unshared electron pair; non-bonding pair of electrons

How can you tell how many bonds and how many lone pairs an atom will have?

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### Count the Valence Electrons!

<table>
<thead>
<tr>
<th>neutral atom</th>
<th># valence e–s</th>
<th># bonds</th>
<th># lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>F</td>
<td>7</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

- Second row elements want to be surrounded by eight valence electrons (an octet).

**e.g.** Carbon wants four more electrons (4 bonds).

\[ \text{Carbon wants four more electrons (4 bonds).} \]

**e.g.** Nitrogen wants three more electrons (three bonds, one lone pair).
1. Multiple Bonding

- Two atoms can share more than one pair of electrons to gain a filled shell (very common in organic molecules)

**Example 1:** Ethylene (C₂H₄)

\[
2 \cdot \text{C} - \bullet + 4 \cdot \text{H} \rightarrow \begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{H}
\end{array}
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\Rightarrow \text{H} = \text{C} - \text{C} \quad \text{double bond: 2 pairs of electrons}
\]

**Example 2:** Acetylene (C₂H₂)

\[
2 \cdot \text{C} - \bullet + 2 \cdot \text{H} \rightarrow \begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\Rightarrow \text{H} = \text{C} \equiv \text{C} - \text{H} \quad \text{triple bond: 3 pairs of electrons}
\]

- Each line represents one shared electron pair.

2. Formal Charge

- Not all atoms are neutral in a Lewis or Kekule structure
- Formal charges help chemists to keep track of the placement of electrons in molecules
- Does not indicate that all of the charge is actually localized on one atom

**Formal Charge Formula:**

\[
\text{Formal Charge} = (\text{group #}) - (\# \text{ non-bonding e}^-) - \frac{1}{2} (\# \text{ shared e}^-)
\]

**Example:** [H₃C–OH₂]⁺

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\Rightarrow \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\quad \text{C: F.C.} = 4 - 0 - 4 = 0
\]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\Rightarrow \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\quad \text{O: F.C.} = 6 - 2 - 3 = +1
\]

Oxygen is charged.

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\Rightarrow \begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\begin{array}{c}
\text{H}
\end{array}
\quad \text{H}_3\text{C} = \text{O} \quad \text{O} \quad \text{H}_2
\]

Always indicate formal charge on problem sets and exams!
Summary of Bonding (Charged Atoms)

C. Short-Hand for Chemists: Easy Communication

1. Line-Angle Formulas: Drawing Complex Molecules Quickly

Propane (pretty easy)

Testosterone (not so easy)

much easier!

Brevetoxin A (!!)
Rules for Drawing Line-Angle Formulas

- Bonds are represented by lines (one line = two shared electrons)
- Do not draw carbon or hydrogen atoms, except at termini (for aesthetics)
- Assume carbon atoms are at ends of lines and where they meet
- Assume enough C–H bonds to give each carbon atom four bonds (an octet)
- Draw heteroatoms and attached hydrogen atoms (N,O,S,P,F,Cl,Br,I, etc.)

e.g. isopropanol: \( \text{CH}_3\text{CH(OH)}\text{CH}_3 \)

e.g. cyclohexanone

2. Using Dashes and Wedges: Molecules Are Not Flat!

- Tetra-Substituted Carbon Is Tetrahedral (more on this later).

\( \text{CH}_4 \)

methane

\( 109.5^\circ \)

lines: in the plane of the paper
dashes: going back into the paper (away from you)
wedges: coming out of the paper (toward you)

e.g. Propane

e.g. Isomers of 1,2-Cyclohexanediol
Representing Molecules

**Lewis/Kekule Structures:** Represent atoms sharing electrons to form bonds

**Line-Angle Structures:** Simplify the drawing of complex molecular structures

**Dashes and Wedges:** Allow chemists to draw molecules in 3-D

_BUT!_ These simplified structures do not accurately represent the electronic nature or reactivity of organic molecules!

It helps to think about electrons in motion . . .

BUT HOW DO WE REPRESENT ELECTRONS IN MOTION?

---

3. **Curved Arrow Formalism (Arrow Pushing)**

- Chemists use arrows to represent the motion of electrons within and between molecules.

<table>
<thead>
<tr>
<th>Arrow Type</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double Arrow</td>
<td>2 electrons moving</td>
<td><img src="example.png" alt="Double Arrow Example" /></td>
</tr>
<tr>
<td>Fishhook Arrow</td>
<td>1 electron moving</td>
<td><img src="example.png" alt="Fishhook Arrow Example" /></td>
</tr>
</tbody>
</table>

1. The tail starts at the electrons that are moving (lone pair or bond).
2. The head shows where the electrons end up (lone pair or bond).

**e.g. electron motion in a substitution reaction** (much more detail later)

![Substitution Reaction Example](example.png)

(l.p. to bond)  
(bond to l.p.)
Sample Problem: Using What You Know

• Use what you know about Lewis bonding to predict the product of the following reaction. Remember to indicate formal charge. Use curved arrows to show the mechanism (movement of electrons).

\[
\text{H}_3\text{N} \quad \gets \quad \text{BH}_3 \quad \rightarrow \quad ?
\]

- Nitrogen atom is nucleophilic (nuclei-loving).

**nucleophile**: electron-rich atom, often negatively charged, with a free lone pair to donate to another atom

- Boron atom is electrophilic (electron-loving).

**electrophile**: electron-poor atom with a low-lying vacant or easily vacated orbital; wants to accept electrons from a nucleophile

\[
\begin{align*}
\text{H}_3\text{N} & \quad \rightarrow \quad \text{BH}_3 \\
\text{H}_3\text{N} & \quad \rightarrow \quad \text{BH}_3
\end{align*}
\]

Formal Charge:
- N: \(5 - 0 - 4 = +1\)
- B: \(3 - 0 - 4 = -1\)

- Chemical reactions generally involve the movement of electrons between two or more molecules, **but electrons also move within a molecule**.

II. Resonance: Electronic Motion Within a Molecule

- The reactivity of a molecule is not always explained by one Lewis structure.
- Molecules can be thought of as **hybrids** or weighted averages of two or more Lewis structures, each with a different placement of electrons.
- These structures, called **resonance structures**, are not real or detectable, but they are a useful conceptual tool for understanding the reactivity of molecules.
e.g. How can you predict where a nucleophile (such as H₂N⁻) will react with formaldehyde (CH₂O)?

\[ \text{H}_2\text{N}^- + \text{CH}_2\text{O} \rightarrow ? \]

- Use resonance to better understand the electronic nature of formaldehyde . . .

\[ \text{H}^+ \text{H} \quad \text{H}^+ \text{H} \quad \text{H}^+ \text{H} \]

- The minor resonance structure suggests that the carbon atom is electron-deficient (electrophilic).

The nucleophile will react with the electrophilic carbon atom.

\[ \text{H}_2\text{N}^- \quad \text{H}^+\text{H} \quad \text{H}_2\text{N}^- \]

A. Rules for Drawing Resonance Structures

1. **Only electrons move!** Nuclei and the sigma- (single bond-) framework are unchanged (Resonance occurs in the pi-system: conjugated lone pairs and pi-bonds).
2. Every resonance structure must be a **valid Lewis structure**.
3. Keep track of **lone pairs** and **formal charges**.
4. Use **arrow-pushing formalism** to interconvert and identify possible resonance structures.
5. Always use **double-headed arrow** (\(\leftrightarrow\)) in between resonance structures.
6. **Lower energy** resonance structures **contribute most** to the overall structure of the molecule.

How do you predict the relative energies of resonance structures?
B. Guidelines for Predicting Energies of Resonance Structures
(In Order of Importance)

i) **Filled Octets**: Second row elements (C, N, O, F) want an octet (filled valence shell of electrons). Because C is the least electronegative, structures in which C has 6 electrons, 3 bonds and a positive charge are possible (not possible with N, O, F).

ii) **Negative charges** on most electronegative atoms.

iii) **Minimize charge separation.**

![Diagram showing resonance structures and their guidelines]

A: follows guidelines
B: violates iii: 2 formal charges
C: violates ii & iii: negative charge on C; 2 formal charges
D: violates i & iii: 6 electrons on C; 2 formal charges
E: violates i & iii: 6 electrons on C; 2 formal charges

Relative Energy: A << B < C << D ~ E
Relative Importance: A (major) > B > C > D ~ E
Delocalization of Charge = Stabilization

- The conjugate base of phenol (phenoxide) is stabilized by resonance.
- Because phenoxide ion is stabilized, phenol is more acidic than cyclohexanol.

\[
\begin{align*}
\text{phenol} & \quad \text{pK}_a \ 10 \\
\text{cyclohexanol} & \quad \text{pK}_a \ 17
\end{align*}
\]

- In general, the more resonance structures there are, the greater the stabilization.
- Equivalent resonance structures provide more stabilization than inequivalent ones.

C. Structure and Reactivity Info from Resonance Structures

e.g. Benzene

- Drawn this way, benzene appears to have two types of carbon–carbon bonds (single and double).
- Experimental data indicates that all of the carbon–carbon bonds in benzene are equivalent and rather unreactive.
- Benzene is approximately 35 kcal/mol more stable than would be expected because the electrons are delocalized around the ring.