Chapter 1: Structure and Bonding

Trends in Bond Strength and Length

S-character

- **$sp$ hybrid**: \( \frac{\text{one } 2s \text{ orbital}}{\text{two hybrid orbitals}} = 50\% \text{ s-character} \)
- **$sp^2$ hybrid**: \( \frac{\text{one } 2s \text{ orbital}}{\text{three hybrid orbitals}} = 33\% \text{ s-character} \)
- **$sp^3$ hybrid**: \( \frac{\text{one } 2s \text{ orbital}}{\text{four hybrid orbitals}} = 25\% \text{ s-character} \)

Electronegativity Trends

Increasing electronegativity

<table>
<thead>
<tr>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.2</td>
<td>1.8</td>
<td>2.5</td>
<td>3.0</td>
<td>3.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
<td>1.6</td>
<td>1.9</td>
<td>2.2</td>
<td>2.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Question 1:
What orbitals are used to form each of the C-C and C-H bonds in CH₃CH₂CH₃ (propane)? How many sigma bonds are present in this molecule (Problem 1.29, third edition)?

Question 2: Label the polar bonds in each molecule. Indicate the direction of the net dipole if there is one (Problem 1.81, third edition).

a. CHBr₃  
b. CH₃CH₂OCH₂CH₃  
c. CBr₄  
d. O=C\begin{array}{c} \text{CH₃} \\
\text{CH₃} \\
\end{array} 

e. \begin{array}{c} \text{Br} \\
\text{Br} \\
\end{array} 

f. \begin{array}{c} \text{Cl} \\
\text{Cl} \\
\end{array}
Chapter 2: Acids and Bases

Factors Determining Acidity

<table>
<thead>
<tr>
<th>Factor</th>
<th>Example</th>
<th>Increasing acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. <strong>Element effects:</strong> The acidity of H−A increases both left-to-right across a row and down a column of the periodic table.</td>
<td><img src="image" alt="Diagram" /></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Carbon" /> − <img src="image" alt="Hydrogen" /></td>
<td><img src="image" alt="Nitrogen" /> − <img src="image" alt="Hydrogen" /></td>
<td><img src="image" alt="Oxygen" /> − <img src="image" alt="Hydrogen" /></td>
</tr>
<tr>
<td>2. <strong>Inductive effects:</strong> The acidity of H−A increases with the presence of electron-withdrawing groups in A.</td>
<td>CH₃CH₂O−H</td>
<td>CF₃CH₂O−H</td>
</tr>
<tr>
<td>3. <strong>Resonance effects:</strong> The acidity of H−A increases when the conjugate base A⁻ is resonance stabilized.</td>
<td>CH₃CH₂O−H</td>
<td>CH₃COO−H</td>
</tr>
<tr>
<td>4. <strong>Hybridization effects:</strong> The acidity of H−A increases as the percent s-character of A⁻ increases.</td>
<td>CH₃CH₃</td>
<td>CH₂=CH₂</td>
</tr>
</tbody>
</table>

**Pka Values (Memorize)**

<table>
<thead>
<tr>
<th>Table 2.1 Selected pKₐ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
</tr>
<tr>
<td>H−Cl</td>
</tr>
<tr>
<td>CH₃COO−H</td>
</tr>
<tr>
<td>HO−H</td>
</tr>
<tr>
<td>CH₃CH₂O−H</td>
</tr>
<tr>
<td>HC≡CH</td>
</tr>
<tr>
<td>H−H</td>
</tr>
<tr>
<td>H₂N−H</td>
</tr>
<tr>
<td>CH₂=CH₂</td>
</tr>
<tr>
<td>CH₃−H</td>
</tr>
</tbody>
</table>
Question 3: Draw the products of each reaction and determine the direction of equilibrium (Problem 2.12, third edition).

- a. \( CH_2=CH_2 + H^- \rightleftharpoons \)
- b. \( CH_4 + OH^- \rightleftharpoons \)
- c. \( CH_3COOH + CH_3CH_2O^- \rightleftharpoons \)
- d. \( Cl^- + CH_3CH_2OH \rightleftharpoons \)

Question 4: Rank the compounds in each group in order of increasing acidity (Problem 2.24, third edition).

- a. \( CH_3CH_2CH_3, CH_3CH_2OH, CH_3CH_2NH_2 \)
- b. \( BrCH_2COOH, CH_3CH_2COOH, CH_3CH_2CH_2OH \)
- c. \( CH_3CH_2NH_2, (CH_3)_3N, CH_3CH_2OH \)
### Chapter 3: Organic Molecules and Functional Groups

#### Table of Functional Groups

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>General structure</th>
<th>Example</th>
<th>Condensed structure</th>
<th>3-D structure</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehyde</td>
<td><img src="image1" alt="Aldehyde structure" /></td>
<td><img src="image2" alt="Aldehyde example" /></td>
<td>CH₃CHO</td>
<td><img src="image3" alt="Aldehyde 3D" /></td>
<td><img src="image4" alt="Aldehyde functional group" /></td>
</tr>
<tr>
<td>Ketone</td>
<td><img src="image5" alt="Ketone structure" /></td>
<td><img src="image6" alt="Ketone example" /></td>
<td>(CH₃)₂CO</td>
<td><img src="image7" alt="Ketone 3D" /></td>
<td><img src="image8" alt="Ketone functional group" /></td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td><img src="image9" alt="Carboxylic acid structure" /></td>
<td><img src="image10" alt="Carboxylic acid example" /></td>
<td>CH₃CO₂H</td>
<td><img src="image11" alt="Carboxylic acid 3D" /></td>
<td><img src="image12" alt="Carboxylic acid functional group" /></td>
</tr>
<tr>
<td>Ester</td>
<td><img src="image13" alt="Ester structure" /></td>
<td><img src="image14" alt="Ester example" /></td>
<td>CH₃CO₂CH₃</td>
<td><img src="image15" alt="Ester 3D" /></td>
<td><img src="image16" alt="Ester functional group" /></td>
</tr>
<tr>
<td>Amide</td>
<td><img src="image17" alt="Amide structure" /></td>
<td><img src="image18" alt="Amide example" /></td>
<td>CH₃CONH₂</td>
<td><img src="image19" alt="Amide 3D" /></td>
<td><img src="image20" alt="Amide functional group" /></td>
</tr>
<tr>
<td>Acid chloride</td>
<td><img src="image21" alt="Acid chloride structure" /></td>
<td><img src="image22" alt="Acid chloride example" /></td>
<td>CH₃COCl</td>
<td><img src="image23" alt="Acid chloride 3D" /></td>
<td><img src="image24" alt="Acid chloride functional group" /></td>
</tr>
</tbody>
</table>
Question 5: Functional groups Trivia

a) One of the most basic functional groups involves only carbon-carbon double bonds. What is this group called?

b) Simply consisting of a C to O double bond (with two R groups bonded to the carbon), this functional group is present in many sugars.

c) This group consists of a nitrogen atom bonded to three R groups.

d) Also a woman's name, this functional group consists of a carbon double bonded to one oxygen and single bonded to another (where both the single-bonded oxygen and carbon are bonded to R groups).

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

f) \[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\]
Types of Intermolecular Forces

Table 3.4 Summary of Types of Intermolecular Forces

<table>
<thead>
<tr>
<th>Type of force</th>
<th>Relative strength</th>
<th>Exhibited by</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>weak</td>
<td>all molecules</td>
<td>CH₃CH₂CH₃CH₂CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₂CH₂CH₂CHO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₃CH₂CH₂CH₂OH</td>
</tr>
<tr>
<td>dipole–dipole</td>
<td>moderate</td>
<td>molecules with a net dipole</td>
<td>CH₂CH₂CH₂CHO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₃CH₂CH₂CH₂OH</td>
</tr>
<tr>
<td>hydrogen bonding</td>
<td>strong</td>
<td>molecules with an O–H, N–H, or H–F bond</td>
<td>CH₃CH₂CH₂CH₂OH</td>
</tr>
<tr>
<td>ion–ion</td>
<td>very strong</td>
<td>ionic compounds</td>
<td>NaCl, LiF</td>
</tr>
</tbody>
</table>

Question 6: Which compound in each pair has the higher boiling point (Problem 3.6, third edition)?

a. (CH₃)₂C=CH₂ or (CH₃)₂C=O
b. CH₃CH₂COOH or CH₃COOCH₃
c. CH₃(CH₂)₄CH₃ or CH₃(CH₂)₅CH₃
d. CH₂=CHCl or CH₂=CHI

Chapter 4: Alkanes, Acyclic and Cyclic Molecules, Nomenclature

Example of how to name compounds:

Sample Problem 4.3 Give the structure corresponding to the following IUPAC name: 6-isopropyl-3,3,7-trimethyldecane.

Solution
Follow three steps to derive a structure from a name.

Step [1] Identify the parent name and functional group found at the end of the name.

decane  →  10 C’s  →  C–C–C–C–C–C–C–C–C–C
Step [2] Number the carbon skeleton in *either* direction.

```
  1 2 3 4 5 6 7 8 9 10
C-C-C-C-C-C-C-C-C-C
```

Step [3] Add the substituents at the appropriate carbons.

---

**Question 7:** Give the structure corresponding to each IUPAC name (Problem 4.12).

- a. 3-methylhexane
- b. 3,3-dimethylpentane
- c. 3,5,5-trimethyloctane
- d. 3-ethyl-4-methylhexane
- e. 3-ethyl-5-isobutylnonane
Chapter 5: Stereochemistry

- Constitutional (or structural) isomers differ in the way the atoms are connected to each other.
- Stereoisomers differ only in the way atoms are oriented in space.
- A Molecule (or object) that is not superimposable on its mirror image is said to be chiral.
- Enantiomers are mirror images that are not superimposable.
- A meso compound is an achiral compound that contains tetrahedral stereogenic centers. Meso compounds generally have a plane of symmetry.
- Because two enantiomers have identical physical properties, they cannot be separated by common physical techniques like distillation.
- Diastereomers and constitutional isomers have different physical properties, and therefore they can be separated by common physical techniques.
- Two enantiomers have exactly the same chemical properties except for their reaction with chiral, non-racemic reagents.

Equations

- Specific rotation (5.12C):  
  \[ \text{specific rotation} = [\alpha] = \frac{\alpha}{l \times c} \]
  \[ \alpha = \text{observed rotation (°)} \]
  \[ l = \text{length of sample tube (dm)} \]
  \[ c = \text{concentration (g/mL)} \]
  \[ dm = \text{decimeter} \]
  \[ 1 \text{ dm} = 10 \text{ cm} \]

- Enantiomeric excess (5.12D):  
  \[ \text{ee} = \% \text{ of one enantiomer} - \% \text{ of the other enantiomer} \]
  \[ = \frac{[\alpha] \text{ mixture}}{[\alpha] \text{ pure enantiomer}} \times 100\% \]
Question 8: How are the compounds in each pair related to each other? Are they identical, enantiomers, diastereomers, constitutional isomers, or not isomers of each other? (5.62 3rd ed)

Question 9: Label the stereogenic center(s) as R or S (5.49 C, 3rd ed)

enalapril
Trade name: Vasotec
Chapter 6: Understanding Organic Reactions

**Image 1 - Energy Diagram**

- Transition state
- $E_p$ determines the rate.
- $\Delta H^\circ$ is the difference in bonding energy between the reactants and products.

**Image 2 - Types of Reactions**

1. **Substitution**
   \[ C - Z + Y \rightarrow C - Y + Z \]
   Where $Z = H$ or a heteroatom. $Y$ replaces $Z$.

2. **Elimination**
   \[ C - C \ (	ext{reagent}) \rightarrow C = C + X - Y \]
   Two $\pi$ bonds are broken. $X$ forms a $\pi$ bond.

3. **Addition**
   \[ \text{reactant} \rightarrow C - C + X - Y \]
   This $\pi$ bond is broken. Two $\sigma$ bonds are formed.

**Image 3 - Trends**

<table>
<thead>
<tr>
<th>Values compared</th>
<th>Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond dissociation energy and bond strength</td>
<td>The higher the bond dissociation energy, the stronger the bond (6.4).</td>
</tr>
<tr>
<td>Energy and stability $E_a$ and reaction rate $E_r$</td>
<td>The higher the energy, the less stable the species (6.5A).</td>
</tr>
<tr>
<td>$E_r$ and reaction rate $E_r$</td>
<td>The larger the energy of activation, the slower the reaction (6.9A).</td>
</tr>
<tr>
<td>$E_r$ and rate constant $k_r$</td>
<td>The larger the energy of activation, the smaller the rate constant (6.9B).</td>
</tr>
</tbody>
</table>

**Image 4 - Equations**

\[ \Delta G^\circ = -2.303 R T \log K_{eq} \]

$K_{eq}$ depends on the energy difference between reactants and products.

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

- $\Delta G^\circ$: Free energy change
- $\Delta H^\circ$: Change in bonding energy
- $\Delta S^\circ$: Change in disorder

\[ R = 8.314 \text{ J/(K\cdot mol)}, T = \text{Kelvin temperature (K)} \]

**Image 5 - Variables**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{eq}$</td>
<td>$K_{eq} &gt; 1$</td>
<td>More products than reactants are present at equilibrium.</td>
</tr>
<tr>
<td>$\Delta G^\circ$</td>
<td>$\Delta G^\circ &lt; 0$</td>
<td>The free energy of the products is lower than the energy of the reactants.</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td>$\Delta H^\circ &lt; 0$</td>
<td>Bonds in the products are stronger than bonds in the reactants.</td>
</tr>
<tr>
<td>$\Delta S^\circ$</td>
<td>$\Delta S^\circ &gt; 0$</td>
<td>The products are more disordered than the reactants.</td>
</tr>
</tbody>
</table>
Question 10: Consider the following energy diagram for the overall reaction: \((\text{CH}_3)_3\text{COH} + \text{HI} \rightarrow (\text{CH}_3)_3\text{Cl} + \text{H}_2\text{O}\). (6.49 3rd ed)

a. How many steps are in the reaction mechanism?

b. Label the \(E_a\) and \(\Delta H^\circ\) for each step, and the \(\Delta H^\circ\) overall for the reaction.

c. Which step is rate-determining? Why?
Question 11: Calculate $\Delta H^\circ$ for each reaction. (6.33 3rd ed)

\[
\text{CH}_3\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{Br} + \text{H}_2\text{O}
\]

\[
\text{Br}\cdot + \text{CH}_4 \rightarrow \text{H}\cdot + \text{CH}_3\text{Br}
\]
Chapter 13: Mass Spectrometry and Infrared Spectroscopy

Mass Spectrometry (MS; 13.1-13.4)
- Mass spectrometry measures the molecular weight of a compound (13.1A).
- The mass of the molecular ion (M) = the molecular weight of a compound. Except for isotope peaks at M + 1 and M + 2, the molecular ion has the highest mass in a mass spectrum (13.1A).
- The base peak is the tallest peak in a mass spectrum (13.1A).
- A compound with an odd number of N atoms gives an odd molecular ion. A compound with an even number of N atoms (including zero) gives an even molecular ion (13.1B).
- Organic monochlorides show two peaks for the molecular ion (M and M + 2) in a 3:1 ratio (13.2).
- Organic monobromides show two peaks for the molecular ion (M and M + 2) in a 1:1 ratio (13.2).
- The fragmentation of radical cations formed in a mass spectrometer gives lower molecular weight fragments, often characteristic of a functional group (13.3).
- High-resolution mass spectrometry gives the molecular formula of a compound (13.4A).

Infrared Spectroscopy (IR; 13.6 and 13.7)
- Infrared spectroscopy identifies functional groups.
- IR absorptions are reported in wavenumbers, $\bar{\nu} = 1/\lambda$.
- The functional group region from 4000-1500 cm$^{-1}$ is the most useful region of an IR spectrum.
- C–H, O–H, and N–H bonds absorb at high frequencies, $\geq 2500$ cm$^{-1}$.
- As bond strength increases, the $\bar{\nu}$ of absorption increases; thus, triple bonds absorb at higher $\bar{\nu}$ than double bonds.

\[
\begin{align*}
\text{C=O} & \quad \sim 1650 \text{ cm}^{-1} \\
\text{C=C} & \quad \sim 2250 \text{ cm}^{-1}
\end{align*}
\]

Increasing bond strength
Increasing $\bar{\nu}$

- The higher the percent s-character, the stronger the bond, and the higher the $\bar{\nu}$ of an IR absorption.

\[
\begin{align*}
\text{C} & \quad \sim \text{H} \\
\text{C}_2\text{H}_3 & \quad \sim \text{H} \\
\text{C}_2\text{H}_5 & \quad \sim \text{H}
\end{align*}
\]

25% s-character 3000-2850 cm$^{-1}$
33% s-character 3150-3000 cm$^{-1}$
50% s-character 3300 cm$^{-1}$

Increasing percent s-character
Increasing $\bar{\nu}$
Question 12: Which compound belongs to the Mass Spec below (13.25 3rd ed)
**Question 13:** Reaction of BrCH₂CH₂CH₂CH₂NH₂ with NaH forms compound W, which gives the IR and mass spectra shown below. Propose a structure for W and draw a stepwise mechanism that accounts for its formation. (13.52 3rd ed)
Chapter 14: NMR

**1H NMR Spectroscopy**

1. The number of signals equals the number of different types of protons (14.2).
2. The position of a signal (its chemical shift) is determined by shielding and deshielding effects.
   - Shielding shifts an absorption upfield; deshielding shifts an absorption downfield.
   - Electronegative atoms withdraw electron density, deshield a nucleus, and shift an absorption downfield (14.3).

- Loosely held π electrons can either shield or deshield a nucleus. Protons on benzene rings and double bonds are deshielded and absorb downfield, whereas protons on triple bonds are shielded and absorb upfield (14.4).

3. The area under an NMR signal is proportional to the number of absorbing protons (14.5).
   - Equivalent protons do not split each other’s signals.
   - A set of n nonequivalent protons on the same carbon or adjacent carbons splits an NMR signal into \( n + 1 \) peaks.
   - OH and NH protons do not cause splitting (14.9).
   - When an absorbing proton has two sets of nearby nonequivalent protons that are equivalent to each other, use the \( n + 1 \) rule to determine splitting.
   - When an absorbing proton has two sets of nearby nonequivalent protons that are not equivalent to each other, the number of peaks in the NMR signal = \( (n + 1)(m + 1) \). In flexible alkyl chains, peak overlap often occurs, resulting in \( n + m + 1 \) peaks in an NMR signal.

**Question 14:** How many different types of protons are present in each compound? (14.34 3rd ed)

\[(\text{CH}_3)_3\text{CH}\]
Question 15: Treatment of 2-butanone (CH₃COCH₂CH₃) with a strong base followed by CH₃I forms a compound Q, which gives a molecular ion in its mass spectrum at 86. The IR (> 1500 cm⁻¹ only) and ¹H NMR spectrum of Q are given below. What is the structure of Q? (14.66 3rd ed)