Chapter 2. Alkanes and Cycloalkanes: Introduction to Hydrocarbons

2.1: Classes of Hydrocarbons

molecules that are made up of carbon and hydrogen

1. Aliphatic
   a. alkanes - contain C-C single bonds - \( C_n H_{(2n+2)} \) saturated hydrocarbons
   b. alkenes - contain C=C double bonds - \( C_n H_{(2n)} \)
   c. alkynes - contain C≡C triple bonds - \( C_n H_{(2n-2)} \)

2. Arenes (aromatics) - cyclic hydrocarbons with alternating C-C single and double bonds

2.2: Electron Waves and Chemical Bonds (please read)

2.3: Bonding in \( H_2 \): The Valence Bond Model

electrons in atomic orbitals combine to form electron pairs in molecular orbitals

Sigma \( (\sigma) \) bond - orbital overlap is along internuclear axis

Circular cross-section

(Figure 2.1, p. 60)
Principle of maximum overlap (L. Pauling) - the strength of a bond is directly proportional to the amount of orbital overlap

2.4: Bonding in $\text{H}_2$: The Molecular Orbital Model - Molecular orbitals (MOs) are linear combinations of atomic orbitals (AOs)

LCAO: \# of MOs = \# of AOs

- 436 KJ/mol
- 436 KJ/mol

(Figure 2.6, p. 64)

2.5: Introduction to Alkanes: Methane, Ethane, and Propane

Alkanes have the general formula $\text{C}_n\text{H}_{2n+2}$

Methane
(CH$_4$)

Ethane
(C$_2$H$_6$)

Propane
(C$_3$H$_8$)

bp= -160° C

bp= -89° C

bp= -42° C

C-C bond length = 153 pm
C-H bond length = 111 pm
Bond angles between 109 - 112° (tetrahedral geometry)

(Figure 2.7, p. 64)
2.6: \( sp^3 \) Hybridization and Bonding in Methane

Energy

\[
\begin{align*}
\text{2p} & \quad \text{2p} \\
\text{2p} & \quad \text{2p} \\
\text{2s} & \quad \text{2s}
\end{align*}
\]

All four \( C-H \) bond of methane are identical

All four \( sp^3 \) hybrid orbital are equivalent

\( sp^3 \) Hybridized Orbitals = 1 part s-orbital + 3 parts p-orbitals

(Figure 2.9, p. 66)

C-H bond strength = 435 KJ/mol
sp\(^3\) hybridized orbital are more directional allowing for greater orbital overlap and strong bonds compared to unhybridized orbitals

### 2.7: Bonding in Ethane

(Figure 2.11, p. 68)

\[ \Delta H^\circ_{C-C} = 376 \text{ KJ/mol} \]

### 2.9: Higher n-Alkanes (please read)

2.10: The C\(_5\)H\(_{12}\) Isomers

**Isomers:** compounds with the same chemical formula, but different arrangement of atoms

**Constitutional isomer:** have different connectivities (not limited to alkanes)

- \( \text{C}_4\text{H}_{10} \)  
  - n-butane  
  - isobutane

- \( \text{C}_5\text{H}_{12} \)  
  - n-pentane  
  - isopentane  
  - neopentane

- \( \text{C}_2\text{H}_5\text{O} \)  
  - butanol

- \( \text{C}_2\text{H}_5\text{O} \)  
  - diethyl ether

**Straight-chain or normal hydrocarbons**  
- n-butane  
- n-pentane

**Branched hydrocarbons**
2.11 - 2.15: Systematic Nomenclature (IUPAC System)

Prefix-Parent-Suffix

Parent- number of carbons
Prefix- substituents
Suffix- functional groups

Naming Alkanes

General Formula: \( C_nH_{2n+2} \)
suffix: -ane

Parent Names:  
(Table 2.2, p. 71)

<table>
<thead>
<tr>
<th>Parent Number</th>
<th>General Formula</th>
<th>Name</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( CH_4 )</td>
<td>Methane</td>
<td>( CH_4 )</td>
</tr>
<tr>
<td>2</td>
<td>( CH_3CH_3 )</td>
<td>Ethane</td>
<td>( C_2H_6 )</td>
</tr>
<tr>
<td>3</td>
<td>( CH_3CH_2CH_3 )</td>
<td>Propane</td>
<td>( C_3H_8 )</td>
</tr>
<tr>
<td>4</td>
<td>( CH_3(CH_2)_2CH_3 )</td>
<td>Butane</td>
<td>( C_4H_{10} )</td>
</tr>
<tr>
<td>5</td>
<td>( CH_3(CH_2)_3CH_3 )</td>
<td>Pentane</td>
<td>( C_5H_{12} )</td>
</tr>
<tr>
<td>6</td>
<td>( CH_3(CH_2)_4CH_3 )</td>
<td>Hexane</td>
<td>( C_6H_{14} )</td>
</tr>
<tr>
<td>7</td>
<td>( CH_3(CH_2)_5CH_3 )</td>
<td>Heptane</td>
<td>( C_7H_{16} )</td>
</tr>
<tr>
<td>8</td>
<td>( CH_3(CH_2)_6CH_3 )</td>
<td>Octane</td>
<td>( C_8H_{18} )</td>
</tr>
<tr>
<td>9</td>
<td>( CH_3(CH_2)_7CH_3 )</td>
<td>Nonane</td>
<td>( C_9H_{20} )</td>
</tr>
<tr>
<td>10</td>
<td>( CH_3(CH_2)_8CH_3 )</td>
<td>Decane</td>
<td>( C_{10}H_{22} )</td>
</tr>
</tbody>
</table>

Alkyl substituents (group): carbon chains which are a substructure of a molecule

R= Rest of the molecule (mainchain)

<table>
<thead>
<tr>
<th>Alkyl Substituents</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CH(_3)-R</td>
<td>Methyl</td>
</tr>
<tr>
<td>2 CH(_3)CH(_2)-R</td>
<td>Ethyl</td>
</tr>
<tr>
<td>3 CH(_3)CH(_2)CH(_2)-R</td>
<td>Propyl</td>
</tr>
<tr>
<td>4 CH(_3)(CH(_2))(_2)CH(_2)-R</td>
<td>Butyl</td>
</tr>
<tr>
<td>5 CH(_3)(CH(_2))(_2)CH(_2)R</td>
<td>Pentyl</td>
</tr>
<tr>
<td>6 CH(_3)(CH(_2))(_3)CH(_2)-R</td>
<td>Hexyl</td>
</tr>
<tr>
<td>7 CH(_3)(CH(_2))(_4)CH(_2)-R</td>
<td>Heptyl</td>
</tr>
<tr>
<td>8 CH(_3)(CH(_2))(_5)CH(_2)-R</td>
<td>Octyl</td>
</tr>
<tr>
<td>9 CH(_3)(CH(_2))(_6)CH(_2)-R</td>
<td>Nonyl</td>
</tr>
<tr>
<td>10 CH(_3)(CH(_2))(_7)CH(_2)-R</td>
<td>Decyl</td>
</tr>
</tbody>
</table>
Rules for Systematic Nomenclature of Alkanes

1. Find the parent chain
   a. Identify the longest continuous carbon chain as the parent chain.
   
   
   7 carbons = hept-

   b. If more than one different chains are of equal length (number of carbons), choose the one with the greater number of branch points (substituents) as the parent.

   2 branch pts.  1 branch pt.

2. Numbering the carbons of the parent chain
   a. Number the carbon atoms of the parent chain so that any branch points have the lowest possible number

   branch pts. at carbons 3 and 4  branch pts. at carbons 4 and 5

   b. If there is branching equidistant from both ends of the parent chain, number so the second branch point has the lowest number.

   branch pts. at carbons 3, 6, 7  branch pts. at carbons 3, 4, 7
3. **Substituents**
   a. Identify and number the substituents and list them in alphabetical order.

   ![Diagram of a molecule with subscripts and labels indicating the positions of substituents.]

   b. If there are two substituents on the same carbon, assign them the same number.

4. **Write out the name**
   a. Write out the name as a single word:
      - hyphens (-) separate prefixes
      - commas (,) separate numbers
   b. Substituents are listed in alphabetical order
   c. If two or more identical substituents are present use the prefixes:
      - di- for two
      - tri- for three
      - tetra- for four

   ![Diagram of a molecule with labeled substituents and numbers indicating their positions.]

   **Note:** These prefixes (di-, tri-, tetra-, etc.) are not used for alphabetizing purposes.

5. **Complex Substituents (substituents with branching)**
   a. Named by applying the four previous rules with some modification
   b. Number the complex substituent separately from the parent.
      Begin numbering at the point of attachment to the parent chain
   c. Complex substituents are set off by parenthesis.

   ![Diagram of a molecule with labeled substituents and numbers indicating their positions, including complex substituents with branching.]
Iso- and neo are part of the alkyl group name and are used for alphabetizing.

**Nonsystematic (trivial) Names:**

**3-carbons:**

```
H2C
H2C
Parent Chain
```

**4-Carbons:**

```
H2C
H2C
Parent Chain
```

sec-butyl- (1-methylpropyl)

```
H2C
H2C
Parent Chain
```

iso-butyl- (2-methylpropyl)

```
H2C
H2C
Parent Chain
```

tert-butyl- (1,1-dimethylpropyl)

**5-Carbons:**

```
H2C
H2C
H2C
Parent Chain
```

isopentyl- (3-methylbutyl)

```
H2C
H2C
H2C
Parent Chain
```

neopentyl- (2,2-dimethylpropyl)

```
H2C
H2C
H2C
Parent Chain
```

tert-pentyl- tert-amyl (1,1,3-trimethylpropyl)

**Alphabetizing trivial names:**

Iso- and neo are part of the alkyl group name and are used for alphabetizing.
sec- and tert- are not included in the alphabetical order.

```
4-(1-methylpropyl)octane on 4-isopropylheptane
```

```
2-methyl-1,2-dimethylpropyldecane on 6-isobutyl-3-methyldecane
```

**Cycloalkanes**

- **Propane**
- **Cyclopropane**
- **Parent Chain**
- **Heptane**
- **Cycloheptane**
- **Cycloheptyl**
- **Octane**
- **Cyclooctane**
- **Cyclooctyl**
- **Nonane**
- **Cyclononane**
- **Cyclononyl**
- **Decane**
- **Cyclodecane**
- **Cyclodecyl**
Naming Cycloalkanes

1. Parent Chain
   a. Use the cycloalkane as the parent chain if it has a greater number of carbons than any alkyl substituent.
   b. If an alkyl chain off the cycloalkane has a greater number of carbons, then use the alkyl chain as the parent and the cycloalkane as a cycloalkyl- substituent.

2. Numbering the Cycloalkane
   a. When numbering the carbons of a cycloalkane, start with a substituted carbon so that the substituted carbons have the lowest numbers (sum).

   Halogen Substituents
   Halogen substituents are treated exactly like alkyl groups:
   -F fluoro-
   -Cl chloro-
   -Br bromo-
   -I iodo-

   1-Chloro-2-methylcyclobutane
Degrees of Substitution

Primary (1°) Carbon: carbon that is bonded to only one other carbon
Secondary (2°) Carbon: carbon that is bonded to two other carbons
Tertiary (3°) Carbon: carbon that is bonded to three other carbons
Quaternary (4°) Carbon: carbon that is bonded to four other carbons

1° Hydrogens- hydrogens on a primary carbon. -CH₃ (methyl group)
2° Hydrogens- hydrogens on a secondary carbon. -CH₂- (methylene group)
3° Hydrogens- hydrogens on a tertiary carbon. CH (methine group)

2.16: Sources of Alkanes and Cycloalkanes (please read)
2.17: Physical Properties of Alkanes and Cycloalkanes
Non-nonbonding intermolecular attractive forces
(van der Waals forces)
1. Dipole – Dipole
2. Dipole – Induced-dipole
3. Induced-dipole – Induced-dipole: small instantaneous dipoles that result from a distortion of the electron clouds. There is an attraction between molecules as result of these temporary dipoles
Alkanes show: regular increase in bp and mp as the molecular weight increase. Branching lowers the bp or alkanes

- n-pentane bp = 36.1 °C
- iso-pentane bp = 27.9 °C
- neo-pentane bp = 9.5 °C

Alkanes have low polarity and are hydrophobic (low water solubility). Solubility decreases are the number of carbons increase

2.18: Chemical Properties: Combustion of Alkanes

Hydrocarbons (C-H bonds) are weak to extremely weak acids

Combustion of hydrocarbons (Oxidation)

\[ C_nH_{2n+2} + O_2 \rightarrow n\ CO_2 + (n+1)\ H_2O + \text{heat} \]

Heat (\(\Delta H^\circ\)) of combustion = \(H^\circ\) (products) - \(H^\circ\) (reactants)

Measure of relative stability

2.19: Oxidation-Reduction in Organic Chemistry

**Oxidation** [O]: the loss of electrons.
- Increase in the number of C-X bonds, where X is an atom more electronegative than carbon. Decrease in H content.

**Reduction** [H]: the gain of electrons.
- Increase in number of C-Y bonds, where Y is an atom less electronegative than carbon. Increase on H content.
Increasing oxidation state

2.20: \(sp^2\) Hybridization and Bonding in Ethylene

hybridize one s-orbital and two p-orbitals

leave one p-orbital unhybridized

Three \(sp^2\) hybrid orbitals and one unhybridized p-orbital

(Figure 2.19, p. 89)
C=C double bonds - ethylene (C₂H₄)

ΔH_C=C° = 611 KJ/mol
ΔH_C-C° = 376 KJ/mol
ΔH_π-bond° = 235 KJ/mol

Molecular Orbitals of C=C

σ-bond + 376 KJ/mol
π-bond + 235 KJ/mol
π-bond - 235 KJ/mol
σ-bond - 376 KJ/mol
2.21: sp Hybridization and Bonding in Acetylene
(Figure 2.22, p. 91)

hybridize one s-orbital and one p-orbitals

leave two p-orbital unhybridized
two sp hybrid orbitals and two unhybridized p-orbitals

C≡C triple bonds- acetylene (C$_2$H$_2$)
one C-C σ-bond and two C-C π-bonds
(Figure 2.23, p. 92)

$\Delta H_{C\equiv C}^\circ = 835 \text{ KJ/mol}$
$\Delta H_{C\equiv C}^\circ = 376 \text{ KJ/mol}$
$\Delta H_{1\text{st }\pi\text{-bond}}^\circ = 235 \text{ KJ/mol}$
$\Delta H_{2\text{nd }\pi\text{-bond}}^\circ = 224 \text{ KJ/mol}$