1.8 \( \text{sp}^2 \) Hybrid Orbitals and the Structure of Ethylene

Ethylene \( \text{C}_2\text{H}_4 \)
- Carbon-carbon double bond
- Four shared electrons
- Planar (flat)
- Bond angles 120°

\( \text{sp}^2 \) hybrid orbitals
- A hybrid orbital derived by combination of an \( s \) atomic orbital with two \( p \) atomic orbitals
- One \( p \) orbital remains non-hybridized

Bonding in Ethylene
- \( \sigma \) bond in ethylene formed by head-on overlap of two \( \text{sp}^2 \) hybrid orbitals
- Two non-hybridized \( 2p \) orbitals overlap sideways forming a \( \pi \) bond
- Carbon-carbon double bond is shorter and stronger than carbon-carbon single bond

Worked Example 1.2

Predicting the Structures of Simple Molecules from Their Formulas

Commonly used in biology as a tissue preservative, formaldehyde, \( \text{CH}_2\text{O} \), contains a carbon-oxygen double bond. Draw the line-bond structure of formaldehyde, and indicate the hybridization of the carbon atom.
1.9  sp Hybrid Orbitals and the Structure of Acetylene

Acetylene C\textsubscript{2}H\textsubscript{2}
- Linear
- Carbon-carbon triple bond
  - Six shared electrons
  - Bond angles are 180°
- sp hybrid orbital
  - A hybrid orbital derived from the combination of one s and one p atomic orbital
  - The two sp hybrids are separated by an angle of 180°
  - Two 2p orbitals remain non-hybridized

---

sp Hybrid Orbitals and the Structure of Acetylene

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond</th>
<th>Bond strength</th>
<th>Bond length (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(kJ/mol)</td>
<td>(kcal/mol)</td>
</tr>
<tr>
<td>Methane, CH\textsubscript{4}</td>
<td>(sp\textsuperscript{3}) C–H</td>
<td>439</td>
<td>105</td>
</tr>
<tr>
<td>Ethane, CH\textsubscript{2}CH\textsubscript{2}</td>
<td>(sp\textsuperscript{3}) C–C (sp\textsuperscript{2})</td>
<td>377</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>(sp\textsuperscript{2}) C–H</td>
<td>428</td>
<td>100</td>
</tr>
<tr>
<td>Ethylene, H\textsubscript{2}C=CH\textsubscript{2}</td>
<td>(sp\textsuperscript{2}) C–C (sp\textsuperscript{2})</td>
<td>728</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>(sp\textsuperscript{2}) C–H</td>
<td>464</td>
<td>111</td>
</tr>
<tr>
<td>Acetylene, H\textsubscript{2}C=CH</td>
<td>(sp\textsuperscript{3}) C=CH (sp\textsuperscript{2})</td>
<td>965</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td>(sp\textsuperscript{1}) C–H</td>
<td>558</td>
<td>133</td>
</tr>
</tbody>
</table>

1.10 Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

Elements other than carbon form covalent bonds using hybrid orbitals

Nitrogen
- Methylamine CH\textsubscript{3}NH\textsubscript{2}
  - Organic derivative of ammonia and the substance responsible for the odor of rotting fish
  - Bond angles are close to the 109.5° tetrahedral angle found in methane
  - Nitrogen hybridizes to form four sp\textsuperscript{3} orbitals
  - One of the four sp\textsuperscript{3} orbitals is occupied by two nonbonding electrons
Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

Oxygen
- Methanol CH₃OH
  - Methyl alcohol
  - Bonds are close to the 109.5° tetrahedral angle
  - Two of the four sp³ hybrid orbitals on oxygen are occupied by nonbonding electron lone pairs

Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

Phosphorus
- Most commonly encountered in biological molecules in organophosphates
  - Compounds that contain a phosphorus atom bonded to four oxygens with one of the oxygens also bonded to carbon
  - Methyl phosphate CH₃PO₃²⁻
    - sp³ hybrid orbitals on phosphorus

Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

Sulfur
- Commonly encountered in biological molecules
  - Thiols
    - Have a sulfur atom bonded to one hydrogen and one carbon
  - Sulfides
    - Have a sulfur atom bonded to two carbons
  - Methanethiol CH₃SH
    - Produced by some bacteria
    - Simplest example of a thiol
    - sp³ hybridization
  - Dimethyl Sulfide (CH₃)₂S
    - Simplest example of a sulfide
    - sp³ hybridization
1.11 The Nature of Chemical Bonds: Molecular Orbital Theory

Molecular Orbital Theory (MO)
- A description of covalent bond formation as resulting from a mathematical combination of atomic orbitals (wave functions) to form molecular orbitals
- Additive combination of two 1s orbitals
  - Leads to formation of a low energy bonding MO
    - Egg shaped
- Subtractive combination of two 1s orbitals
  - Leads to formation of a high energy antibonding MO
    - Elongated dumbbell shaped with a node between the nuclei

The Nature of Chemical Bonds: Molecular Orbital Theory

- Additive combination of two 2p orbitals
  - Leads to formation of a low energy bonding MO
    - The bonding MO is formed by combining p orbital lobes with the same algebraic sign
    - No node between nuclei
- Subtractive combination of two 2p orbitals
  - Leads to formation of a high energy antibonding MO
    - The antibonding MO is formed by combining p orbital lobes with different algebraic signs
    - Node between nuclei
- Only the bonding MO is occupied in ethylene

1.12 Drawing Chemical Structures

Condensed Structures
- A shorthand way of writing structures in which carbon-hydrogen and carbon-carbon bonds are understood rather than explicitly shown
- 2-Methylbutane
Skeletal Structure (Line-Bond Structure)

- A shorthand way of writing structures in which carbon atoms are assumed to be at each intersection of two lines (bonds) and at the end of each line.

Three rules:
1. Carbon atoms not usually shown, they are assumed.
2. Hydrogen atoms bonded to carbon are assumed.
3. Atoms other than carbon and hydrogen are shown.

Note: Sometimes the writing order of atoms is inverted to make bonding connections clearer.

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**TABLE 1.3**

Kekulé and Skeletal Structures for Some Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kekulé structure</th>
<th>Skeletal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene, C₅H₈</td>
<td><img src="image1" alt="Isoprene Kekulé structure" /></td>
<td><img src="image2" alt="Isoprene Skeletal structure" /></td>
</tr>
<tr>
<td>Methylcyclohexane, C₁₉H₃₈</td>
<td><img src="image3" alt="Methylcyclohexane Kekulé structure" /></td>
<td><img src="image4" alt="Methylcyclohexane Skeletal structure" /></td>
</tr>
<tr>
<td>Phenol, C₈H₈O</td>
<td><img src="image5" alt="Phenol Kekulé structure" /></td>
<td><img src="image6" alt="Phenol Skeletal structure" /></td>
</tr>
</tbody>
</table>

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Chapter 2: Polar Covalent Bonds

Problems: 2.1-43, 47-53
Chemical bonds
- **Ionic bonds**
  - Ions held together by electrostatic attractions between unlike charges
  - Bond in sodium chloride
  - Sodium transfers an electron to chlorine to give Na⁺ and Cl⁻
- **Nonpolar Covalent bonds**
  - Two electrons are shared equally by the two bonding atoms
  - Carbon-carbon bond in ethane
  - Symmetrical electron distribution in the bond

Most bonds are neither fully ionic or covalent

Polar Covalent Bonds: Electronegativity

- **Polar covalent bonds**
  - A covalent bond in which the electron distribution between atoms is unsymmetrical
  - Bond polarity is due to difference in electronegativity (EN)

Electronegativity (EN)
- The ability of an atom to attract shared electrons in a covalent bond
- Generally increases across the periodic table from left to right and from bottom to top
• Bonds between atoms whose electronegativities differ by less than 0.5 are nonpolar covalent
• Bonds between atoms whose electronegativities differ by 0.5 to 2.0 are polar covalent
• Bonds between atoms whose electronegativities differ by more than 2.0 are largely ionic

Carbon-hydrogen bonds are nonpolar. Bonds between carbon (EN = 2.5) and more electronegative elements, such as oxygen (EN = 3.5) and nitrogen (EN = 3.0) are polar covalent bonds with the bonding electrons drawn towards the more electronegative atoms.

Electrostatic potential maps
• Show calculated charge distributions
• Colors indicate electron-rich (red; $\delta^-$) and electron-poor (blue; $\delta^+$) regions
• Methanol, CH$_3$OH, has a polar covalent C-O bond, and methyl lithium has a polar covalent C-Li bond
• A crossed arrow is used to indicate direction of bond polarity
• Electrons are displaced in the direction of the arrow

Inductive effect
• The electron-attracting or electron-withdrawing effect transmitted through $\sigma$ bonds. Electronegative elements have an electron-withdrawing inductive effect
• Metals inductively donate electrons
• Reactive nonmetals inductively withdraw electrons
• Inductive effects play a major role in understanding chemical reactivity