Chemical Bonding and Molecular Structure

What are bonds? Why do bonds form?

Valence Electrons:
- Number and distribution of valence e- determines reactivity
- Main Group Elements (s and p block):
- Transition Metals (d block):
- EXAMPLES: Bromine and Iron

Bonding: Ionic vs Covalent Two Extremes

Ionic Bonding:
- Electrostatic attraction
  - Discreet charges... “transferred” electrons
- Modeled using Coulomb’s Law
  \[ F = \frac{Q_1 Q_2}{\varepsilon_0 r^2} \]
  \( Q = \) charge
  \( r = \) separation
  \( \varepsilon_0 = \) dielectric constant

Covalent Bonding:
- Also an electrostatic attraction
  - No charge separation... “shared” electrons
Electronegativity: Essential in understanding bonding and predicting structure.

**Electronegativity:** ability of an atom in a bond (molecule) to attract electrons to itself
- Trends in electronegativity
- Related to Ionization Energy and Electron Affinity
  \[ EN \propto (IE - EA) \]
- What does this mean as far as bonding is concerned?

**Bonding Models**
- Attempts to explain real life (shape, reactivity, properties).
  Sometimes they work better than others. REAL LIFE WINS!

**Using Lewis Dot Structures to Model Molecules**
- Localized electron bonding model
  - Valence electron bookkeeping

  - Primary goal in bond formation:

  - Representing bonding using Lewis structures has two key features:
    1. 
    2. 
  - Best suited for s and p block compounds
    - Particularly up to Ne
Guidelines for Drawing Lewis Structures

Underlying criteria: “Octet Rule”: Kind of like the Pirate Code

General Scheme: (CH₂Cl₂ and CO₂ as examples)
1. Determine arrangement of atoms (skeletal structure)...HOW?
   • Central vs peripheral (terminal) atoms
2. Determine total # of valence e⁻...HOW?
3. Draw single bonds between central atom and each peripheral atom
4. Distribute remaining e⁻ as lone pairs around peripheral atoms until all have an octet
5. Add multiple bonds to central atom if necessary until all atoms have filled octets.
6. Double-check that all e⁻ have been used and that all atoms have filled octets!

Guidelines for Drawing Lewis Structures

Formal Charge (FC)
• Calculated for a specific atom in a molecule
  \[ FC = \text{group} \# - (\# \text{ of e⁻ in lone pairs} + 1/2(\# \text{ of bonding e⁻}) \]
  • IMPORTANT! The sum of all the FC for a species or ion MUST equal the net charge on the species!

Example: Calculate the FC on each atom in CN⁻:

FC can help when drawing Lewis Structures
1. FC on each atom should be as small as possible
2. (-) FC should appear on the most electronegative atoms, (+) FC on least electronegative.
3. FC of the same sign on adjacent atoms is unlikely.
Things to Keep in Mind

Molecules are THREE DIMENSIONAL and real life wins!

- Not everything satisfies the octet rule!
  - Hydrogen is different! (so is boron)
  - Some atoms expand their octets
  - Odd electron species exist! (NO, for example)
  - Transition metals and the octet rule.

- Carbon forms four bonds…usually.

- Isoelectronic Species (i.e. NO⁺, N₂, CO, CN⁻)

- Resonance (Section 10.5)

Bonding, Lewis Structures, and Molecular Shape

Valence Shell Electron Pair Repulsion (VSEPR) model:

- Bonding and lone pairs of electrons repel each other and try to get as far apart as possible

What shapes would we predict? AXₙ or AXₙEₘ models.  (It all starts with Table 10.1)

- X = terminal atoms, E = unshared electron pairs on central atom.
- Suggestion: think of “things” around the central atom.
- Those “things” want to get as far apart in space as possible.
- Unshared pairs take up more room than bonding pairs.
- Electron-pair geometry may be different than molecular geometry
Bonding, Lewis Structures, and Molecular Shape

Case 1: No lone pairs around central atoms
- (don’t worry about lone pairs on peripheral atoms)
- Electron-pair and molecular geometry are the same.

Case 2: Lone pairs on central atom:
- Two things to remember
  1. Lone pairs occupy space (more space than bonding pairs)
  2. Lone pairs repel electrons
- BUT: You predict shape by predicting electron-pair geometry and converting to molecular geometry.
  - Electron-pair and molecular geometry may (and typically are) different.

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**Table 10.1 Molecular Geometry as a Function of Electron-Group Geometry**

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>0</td>
<td>AX₂</td>
<td>X—X</td>
<td>180°</td>
<td>BrCl₂</td>
</tr>
</tbody>
</table>

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*For a discussion of the structure of SO₂, see page 402.
*For a discussion of the placement of the lone-pair electrons in this structure, see page 401.
Bonding, Lewis Structures, and Molecular Shape

• # Things = 3

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>trigonal-planar</td>
<td>0</td>
<td>AX₃</td>
<td>120°</td>
<td>BF₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(trigonal planar)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>AX₂E</td>
<td>120°</td>
<td>SO₂⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(bent)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bonding, Lewis Structures, and Molecular Shape

• # Things = 4

<table>
<thead>
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<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>0</td>
<td>AX₄</td>
<td>109.5°</td>
<td>CH₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(tetrahedral)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>AX₃E</td>
<td>109.5°</td>
<td>NH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(trigonal-pyramidal)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>AX₂E₂</td>
<td>109.5°</td>
<td>CH₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(bent)</td>
<td></td>
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<td></td>
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</tbody>
</table>
### Bonding, Lewis Structures, and Molecular Shape

**# Things = 5**

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>AX₅</td>
<td>90°, 120°</td>
<td>PC₂</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>AX₅³</td>
<td>90°, 120°</td>
<td>BF₃</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>trigonal bipyramidal</td>
<td>AX₃E₂</td>
<td>90°</td>
<td>CH₃</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>trigonal bipyramidal</td>
<td>AX₅E</td>
<td>90°</td>
<td>SF₅</td>
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**# Things = 6**

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<th>Electron-Group Geometry</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>octahedral</td>
<td>AX₆</td>
<td>90°</td>
<td>SF₅</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(octahedral)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>octahedral</td>
<td>AX₆E</td>
<td>90°</td>
<td>BiF₅</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(square-pyramidal)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>octahedral</td>
<td>AX₆E₂</td>
<td>90°</td>
<td>XeF₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(square-planar)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bond and Molecular Polarity

Polar bonds result from unequal sharing of electrons
- Due to electronegativity differences
- Produced bond dipoles.

Just as bonds can be polar, molecules can also be polar
- Molecular polarity plays major role in:
  - solubility (like dissolves like),
  - reactivity (biochemical interactions)

Molecular polarity is determined by polarity and orientation of bonds in the molecule
- Need structure first!

Examples: $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{CCl}_4$

Predicting Molecular Polarity

- Are there polar bonds or nonzero formal charges? Yes → No
- Is the molecule asymmetric? Yes → No
- Are the charges (dipoles) asymmetric? Yes → No

Nonpolar Molecule (no molecular dipole)

Polar Molecule (has molecular dipole)
Bond Characteristics

Bond Order:

Bond Length (Table 10.2):

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length, pm</th>
<th>Bond</th>
<th>Bond Length, pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>79.14</td>
<td>C—C</td>
<td>154</td>
</tr>
<tr>
<td>H—C</td>
<td>110</td>
<td>C≡C</td>
<td>134</td>
</tr>
<tr>
<td>H—N</td>
<td>100</td>
<td>C≡N</td>
<td>120</td>
</tr>
<tr>
<td>H—O</td>
<td>07</td>
<td>C≡O</td>
<td>147</td>
</tr>
<tr>
<td>H—S</td>
<td>132</td>
<td>C≡N</td>
<td>128</td>
</tr>
<tr>
<td>H—F</td>
<td>91.7</td>
<td>C≡N</td>
<td>116</td>
</tr>
<tr>
<td>H—Cl</td>
<td>127.4</td>
<td>C≡O</td>
<td>143</td>
</tr>
<tr>
<td>H—Br</td>
<td>144.4</td>
<td>C≡O</td>
<td>120</td>
</tr>
<tr>
<td>H—I</td>
<td>160.9</td>
<td>C≡Cl</td>
<td>178</td>
</tr>
</tbody>
</table>

Bond Characteristics

Bond Strength (Bond Dissociation Energy, Table 10.3): Useful in predicting thermodynamics

- Bond breaking: _____________ energy
- Bond formation: _____________ energy

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy, kJ/mol</th>
<th>Bond</th>
<th>Bond Energy, kJ/mol</th>
<th>Bond</th>
<th>Bond Energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>436</td>
<td>C—C</td>
<td>347</td>
<td>N—N</td>
<td>163</td>
</tr>
<tr>
<td>H—C</td>
<td>414</td>
<td>C≡C</td>
<td>611</td>
<td>N≡N</td>
<td>418</td>
</tr>
<tr>
<td>H—N</td>
<td>389</td>
<td>C≡N</td>
<td>817</td>
<td>N≡O</td>
<td>946</td>
</tr>
<tr>
<td>H—O</td>
<td>464</td>
<td>C≡N</td>
<td>305</td>
<td>N≡O</td>
<td>222</td>
</tr>
<tr>
<td>H—S</td>
<td>368</td>
<td>C≡N</td>
<td>615</td>
<td>N≡O</td>
<td>590</td>
</tr>
<tr>
<td>H—F</td>
<td>555</td>
<td>C≡N</td>
<td>891</td>
<td>O≡O</td>
<td>142</td>
</tr>
<tr>
<td>H—Cl</td>
<td>431</td>
<td>C≡O</td>
<td>361</td>
<td>O≡O</td>
<td>498</td>
</tr>
<tr>
<td>H—Br</td>
<td>364</td>
<td>C≡O</td>
<td>736b</td>
<td>F—F</td>
<td>159</td>
</tr>
<tr>
<td>H—I</td>
<td>297</td>
<td>C≡Cl</td>
<td>339</td>
<td>Cl—Cl</td>
<td>243</td>
</tr>
</tbody>
</table>

Br—Br 193  I—I 151
Calculating $\Delta H^\circ_{\text{rxn}}$ for gas phase reactions:

- Why Gas Phase?

\[
\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)
\]

<table>
<thead>
<tr>
<th>Lewis Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonds Broken</td>
</tr>
<tr>
<td>Bonds Formed</td>
</tr>
<tr>
<td>Energies (kJ)</td>
</tr>
</tbody>
</table>

\[
\Delta H_{\text{rxn}} = \Delta H_{\text{bonds broken}} - \Delta H_{\text{bonds formed}}
\]

Isomers

- **Isomers**: different compounds with same molecular formula
- **Stereoisomers**: isomers where connections are same, but arrangement in space different
- **Constitutional Isomers**: isomers where atoms are connected differently

**Enantiomers**: stereoisomers that are mirror images
**Diastereomers**: stereoisomers that are not mirror images

**EXAMPLE**: $\text{C}_2\text{H}_2\text{Cl}_2$ has 3 possible structures, only 2 are diastereomers
Enantiomers

Molecules that have Enantiomers are Chiral
- Amino Acids are one Enantiomer
- Some bacteria use the amino acids of the other chirality to trick their hosts

Enantiomers have similar physical properties (nearly identical)
- Interact differently with polarized light
- May have dramatically different reactivity
  - Thalidomide