Bonding: General Concepts

- Ionic Bonds  
  *Sections 13.2 - 13.6*

- Covalent Bonds  
  *Section 13.7*

- Covalent Bond Energy & Chemical Reactions
  - *Section 13.8 - 13.9*

- Lewis Structures  
  *Sections 13.10 - 13.12*

- VSEPR Theory  
  *Section 13.13*  
  **Friday**

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Order of Filling Subshells

*What is the order in which subshells are filled?*

4s level filled before 3d

Figure from *Chemistry the Easy Way* by Joseph A. Mascetta
What is Bond Energy?

- Bond energy is the energy required to make or break 1 mol of a chemical bond.
  - Energy is released when bonds are broken: Exothermic
  - Energy is supplied when bonds are formed: Endothermic

### Bond Energies, kJ/mol

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>432 kJ/mol</td>
<td>C=C</td>
<td>614 kJ/mol</td>
</tr>
<tr>
<td>H—F</td>
<td>565 kJ/mol</td>
<td>C=C</td>
<td>839 kJ/mol</td>
</tr>
<tr>
<td>H—Cl</td>
<td>427 kJ/mol</td>
<td>O=O</td>
<td>495 kJ/mol</td>
</tr>
<tr>
<td>H—Br</td>
<td>363 kJ/mol</td>
<td>C=O*</td>
<td>745 kJ/mol</td>
</tr>
<tr>
<td>H—I</td>
<td>295 kJ/mol</td>
<td>C=O</td>
<td>1072 kJ/mol</td>
</tr>
<tr>
<td>C—H</td>
<td>413 kJ/mol</td>
<td>N=O</td>
<td>607 kJ/mol</td>
</tr>
<tr>
<td>C—C</td>
<td>347 kJ/mol</td>
<td>N=N</td>
<td>418 kJ/mol</td>
</tr>
<tr>
<td>C—N</td>
<td>305 kJ/mol</td>
<td>N=N</td>
<td>941 kJ/mol</td>
</tr>
<tr>
<td>C—O</td>
<td>358 kJ/mol</td>
<td>C=N</td>
<td>615 kJ/mol</td>
</tr>
<tr>
<td>C—F</td>
<td>485 kJ/mol</td>
<td>C≡N</td>
<td>891 kJ/mol</td>
</tr>
</tbody>
</table>

- Higher bond energy
- Single bonds have lower bond energy in general
Table 13.7 Bond Lengths for Selected Bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Type</th>
<th>Bond Length (Å)</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>Single</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>Single</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>C=C</td>
<td>Double</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>C≡O</td>
<td>Single</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>C≡C</td>
<td>Triple</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>C—N</td>
<td>Single</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>Double</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>Triple</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>

Multiple bonds are shorter than single bonds.

What is enthalpy (H)?
- A state function: pathway does not matter
- \( H = E + PV \), where
  - \( E \) = internal energy of a system
  - \( P \) = pressure of the system
  - \( V \) = volume of the system
- \( \Delta H = q_p \), the energy flow as heat at constant pressure

How can enthalpy help us understand chemical bonding?
Bond Enthalpy

- For a chemical reaction, \[ \Delta H = \Sigma \text{Energy}_{\text{bonds broken}} - \Sigma \text{Energy}_{\text{bonds formed}} \]

- Bond enthalpy = \( \Delta H \) in a reaction in which a chemical bond is broken in the gas phase.

\[
\text{CCl}_2F_2 (g) + 2 \text{H}_2(g) \rightarrow \text{CH}_2\text{Cl}_2 (g) + 2 \text{HF}(g)
\]

What is the overall bond enthalpy for this reaction?

Enthalpy of Reaction

More energy is supplied from bond formation than that released from bond breaking. Thus, overall reaction is endothermic.
1. Count # of valence electrons available - “A”

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic #</th>
<th>Shell Occupancy</th>
<th># Valence e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>15</td>
<td>2 + 8 + 5</td>
<td>5</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>2 + 6</td>
<td>6</td>
</tr>
<tr>
<td>Cl</td>
<td>17</td>
<td>2 + 8 + 7</td>
<td>7</td>
</tr>
</tbody>
</table>

SUM = 5 + 6 + (7x3) = 32 valence electrons

2. Count total # of electrons needed - “N”

<table>
<thead>
<tr>
<th>Element</th>
<th># e⁻ Needed</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>8</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
</tr>
<tr>
<td>3Cl’s</td>
<td>24</td>
</tr>
</tbody>
</table>

SUM = 40 valence electrons
3. Calculate # e⁻'s shared: \[ S = (e^- \text{ Needed}) - (e^- \text{ Available}) \]

\[ S = 40 - 32 = 8 \text{ valence electrons shared} \]

4. Draw skeleton w/ shared e⁻ (8 shared electrons)

5. Assign remaining shared electrons as double or triple bonds. (NOT REQ'D IN THIS EXAMPLE)
6. Assign remaining electrons as lone pairs.

7. Calculate the formal charge on each atom

\[
\text{Phosphorus} \quad 5 \quad - \quad 0 \quad - \quad \frac{1}{2} \quad (8)
\]

# valence electrons  # lone pair electrons  # bonding electrons

Formal Charge on Phosphorus: +1
7. Calculate the formal charge on each atom

**Chlorine**

\[
\begin{array}{ccc}
\text{valence electrons} & \text{lone pair electrons} & \text{bonding electrons} \\
7 & 6 & \frac{1}{2} (2)
\end{array}
\]

Formal Charge on Chlorine: 0

**Oxygen**

\[
\begin{array}{ccc}
\text{valence electrons} & \text{lone pair electrons} & \text{bonding electrons} \\
6 & 6 & \frac{1}{2} (2)
\end{array}
\]

Formal Charge on Oxygen: -1
7. Calculate the formal charge on each atom

Write the Lewis structure for $\text{POCl}_3$

Check that formal charges sum to a net charge of 0 for the molecule

$(+1)_{\text{Phosphorus}} + (0)_{\text{Chlorine}} + (-1)_{\text{Oxygen}}$

Formal Charge on the molecule: 0

PRS Question

What does B represent?

1. Attractive forces dominate over repulsive forces.
2. Repulsive forces dominate over attractive forces.
3. Attractive and repulsive forces roughly balance.
4. There are no repulsive or attractive forces.
1. Attractive forces dominate over repulsive forces.
2. Repulsive forces dominate over attractive forces.
3. Attractive and repulsive forces roughly balance.
4. There are no repulsive or attractive forces.

A = in fig represents interspecies separation that is too close together. Energy is relatively high because of repulsive forces.
What does B represent?

**C** = in fig represents interspecies separation that is too far apart. Energy is relatively high. **Attractive** forces cause the species to want to move closer together.

**B** = in fig represents distance at which two species are most energetically stable. At that energy, the attractive forces and the repulsive forces counteract each other. **Correct Answer: 3**
Which of the following bonds has the lowest enthalpy?

1. C\(-\)C
2. C=C
3. C=O
4. C=N

Because single bonds generally have lower bond energies than double bonds.