Upcoming

This week:
  Lab – Beer’s Law
  Exam – Friday (Chapters 6, 7, 8)

Next week:
  No class on Tuesday
  Lab – No lab for Tuesday section
    Molecular Geometry / check out (Wed.)

Following week:
  Lab – Molecular Geometry / check out (Tues.)
  No lab for Wednesday section
Due this week...

- Volumetric Analysis formal lab report:
  - Read the formal lab report direction on pg. 56 in the lab manual
  - Make sure to write answers and procedures in **essay** form – not lists or numbered paragraphs
  - Anything you measure or observe in the lab is “Data”. Anything you calculate from data is reported as a “Result”.
  - Conclusion is a short paragraph where you summarize your results and should echo your purpose.
Lab this week

• Beer’s Law / Analysis of a sports drink
  – Work in pairs
  – Analyze the dye Allura Red
    • At multiple wavelengths
    • At multiple concentrations
    • Using UV-vis spectroscopy
    • Determine \( \lambda_{\text{max}} \)
  – Use what you know to calculate the concentration of red dye in a sports drink (Gatorade, etc.)
Chapter 8: Chemical Bonding and Climate Change

Chemical Bonds

- **Chemical bond** is a term used to characterize an interaction between two atoms that results in a reduction in the energy of the system relative to the isolated atoms.

- The degree of energy reduction or “stabilization” is given by the energy required to break the bond (known as the “bond energy”).

- This stabilization is achieved by the interaction of the electron densities on neighboring atoms.

- For now, we will model chemical bonds as a sharing of electrons through the overlap of atomic orbitals on the bound atoms.
Strictly speaking, an ionic bond is an extreme case of polar covalent, in which the electron pair that defines the bond is much more likely to be found near one of the atoms than near the other.

For simplicity, ionic bonds are often modeled as a transfer of one or more electrons from one atom to the other.
There is one more type of chemical bond:
- The metallic bond: **Metals exist as nuclei surrounded by a sea of electrons.**

The electrons in a metal are shared among all the nuclei, so the electrons are **delocalized** (i.e., not fixed to a specific atom).
Metallic Bonds

• In a metallic bond, the electrons are free to move throughout the solid.
• This is responsible for metals’ unique properties.
  – Pots and pans are usually made of metal because metals conduct heat and electricity as electrons flow through the metal.
  – Metals are malleable and ductile because electrons act as a glue, holding the positively-charged nuclei together → hammered metal and metallic wire.
When Na(s) is put in contact with Cl\textsubscript{2}(g), a rapid and very exothermic reaction occurs, resulting in a white, granular solid.

If this solid is melted, it will conduct electricity, indicating that it contains charged species.
Why the formation of Na\(^+\) and Cl\(^-\)?

In short, Na\(^+\) and Cl\(^-\) are more energetically stable than atomic Na and Cl...we can rationalize this by considering the electronic structure of the ions relative to the atoms:

\[
\text{Na} \cdot + \cdot \text{Cl}: \quad \rightarrow \quad \begin{array}{c}
\text{Na}^+ \\
\text{[Ne]}3s^1 \\
\text{[Ne]}3s^23p^5
\end{array} + \begin{array}{c}
\text{Cl}^- \\
\text{[Ne]} \\
\text{[Ar]}
\end{array} \rightarrow \text{NaCl crystal}
\]

With the transfer of an electron from Na to Cl, two ions of opposite charge and noble-gas electronic structure are produced. The Coulombic attraction between these ions is largely responsible for the stabilization.
In solid NaCl, Coulombic stabilization results in a regular cubic crystal structure. Each ion is surrounded by six ions of the opposite charge.
Properties of Ionic Compounds

• Ionic compounds exist as networks of ions, with cations surrounding anions, and vice versa.
  – To melt ionic compounds, every bond between each Na\(^+\) ion and the Cl\(^-\) ions surrounding it must be broken, as well as bonds between each Cl\(^-\) ion and the Na\(^+\) ions surrounding it.
  – A lot of energy is required to break all of these bonds.
  – Ionic compounds have relatively **high melting points**—much higher than water’s (0°C). **All ionic compounds are solids** at room temperature.
  – Ionic compounds **do not conduct electricity when solid** (ions are fixed in place), but they do **conduct in the molten (liquid) and aqueous states** (ions move around freely).
Covalent Bonds

- Formed when two atoms share electrons with each other.

\[
\begin{align*}
H & \cdot \red{\heartsuit} \cdot H \\
\text{H} & \quad \text{H}
\end{align*}
\]

The driving force for covalent bond formation is to attain a full outer-most electron shell.

Note that this line represents a **pair** of electrons.
The H-H interaction is an example of covalent bonding. The shared electron pair is equally likely to be found at either H atom.
Polar Covalent Bonds

- If ionic bonding is one limit, and covalent bonding is the other limit, what lies in the middle?

**Polar covalent bonds**: bonds in which electrons are shared, but the probability distribution is skewed toward one of the atoms.

HF is a typical example.
**Electronegativity**: the ability of an atom in a molecule to attract shared electrons to itself.

Roughly speaking, the higher an atom’s ionization energy, the higher its electronegativity.
Electronegativity

• To quantify electronegativity, compare the bond energy of an “HX” molecule to that of the average of an HH bond and an XX bond:

\[
\text{Expected H-X energy} = (1/2)[(\text{H-H energy}) + (\text{X-X energy})]
\]

\[
\Delta = (\text{H-X})_{\text{experimental}} - (\text{H-X})_{\text{expected}}
\]

\[
\Delta \sim 0: \text{ nonpolar covalent} \quad \Delta > 0: \text{ polar covalent}
\]

• **Key Idea**: the greater the electronegativity difference between two atoms, the more “ionic” the bond.

• The quantity \( \Delta \) is the electronegativity of atom X, as measured relative to H.
**Example:** Which of the following pairs is expected to demonstrate intermediate bonding behavior (i.e., polar covalent).

<table>
<thead>
<tr>
<th></th>
<th>Cl-Cl</th>
<th>C-H</th>
<th>O-H</th>
<th>Na-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_{\text{elect}} )</td>
<td>0</td>
<td>0.4</td>
<td>1.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

**Note:** The electronegativity of C and H are very similar, so in practice we will assume that C-H bonds are essentially nonpolar.
**Bond Dipoles**

Electrons are shared unequally in polar covalent bonds, resulting in partial atomic charges.

When placed in an electric field, molecules with polar covalent bonds will align... *this indicates that the positive and negative charge centers do not coincide.*

Such a charge separation in a bond is called a **dipole**.

Dipoles are represented with a vector called a **dipole moment**:

\[ \text{center of positive charge} \]
\[ \text{center of negative charge} \]
• Note that what dipole moments and electron density maps **really** represent is the **electron probability distribution** in a bond or molecule.

• In a polar covalent bond, there is a higher probability of finding the electron pair near the atom with the largest electronegativity.

• We can use these ideas to rationalize experimentally-observed reactivity trends.
Ionic vs. Polar Covalent

**Ionic bonds** occur between two atoms with very different ENs.

**Polar covalent bonds** also occur between atoms with different ENs.

So where is the dividing line between “ionic” bonding and “polar covalent” bonding?

In reality, total ionic bonding is probably never achieved, and all “ionic” bonds can be considered to be polar covalent, with varying degrees of ionic character.
We can define the ionic character of bonds as follows:

$$\text{% Ionic Character} = \frac{(\text{dipole moment } X-Y)_{\text{experimental}}}{(\text{dipole moment } X^+Y^-)_{\text{calculated}}} \times 100\%$$

The dipole moment ($\mu$) is defined as:

$$\mu = QR$$

Charge magnitude \quad Separation distance

to calculate this dipole, assume complete transfer of an electron... charge = 1.6 \times 10^{-19} \text{ C}

The units of dipole moment are generally the Debye (D), a "Coulomb" (C) of charge acting over a distance (m):

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C.m}$$
• The experimentally-determined dipole moment of HF is 1.83 D. What is the ionic character of the H-F bond? (bond length = 92 pm)

\[
\mu_{\text{calc}} = (1.6 \times 10^{-19} \text{ C})(9.2 \times 10^{-11} \text{ m})
\]

\[
= 1.5 \times 10^{-29} \text{ C.m} \times (1 \text{D}/3.336 \times 10^{-30} \text{ C.m})
\]

\[
= 4.4 \text{ D}
\]

Theoretical dipole moment of H\(^+\) F\(^-\) pair (complete transfer of one electron)

% Ionic Character = \[
\frac{\mu_{\text{exp}}}{\mu_{\text{calc}}} \times 100% = \frac{1.83 \text{ D}}{4.4 \text{ D}} \times 100% = 42%
\]
% Ionic Character = \frac{(\text{dipole moment } X-Y)_{\text{experimental}}}{(\text{dipole moment } X^+Y^-)_{\text{calculated}}} \times 100\%

Compounds with % ionic character greater than ~50% are typically considered to be ionic.
Range of Chemical Bond Types

Covalent

Polar Covalent

Ionic

Increased Ionic Character
Lewis Dot Structures

- Developed by G. N. Lewis to serve as a way to describe bonding in polyatomic systems. *It’s a method of figuring out what molecules look like.*

- **Central idea**: the most stable arrangement of electrons is one in which all atoms have a “noble” gas configuration.

An atom typically forms as many bonds as it has “holes” in its valence shell.
LDS Mechanics

- Atoms are represented by atomic symbols surrounded by valence electrons.
- Electron pairs between atoms indicate bond formation.
- Bonding pairs are typically represented by a line:

```
  F—F
```
LDS Mechanics (cont.)

• Three steps for “basic” Lewis structures:

  1. Sum the valence electrons for all atoms to determine total number of electrons.

  2. Use pairs of electrons to form a bond between each pair of atoms (bonding pairs).

  3. Arrange remaining electrons around atoms (lone pairs or multiple bonds) to satisfy the “octet rule” for each atom (“duet” rule for hydrogen).
LDS Mechanics (cont.)

• An example: CH₄

\[
\begin{array}{c}
\text{H} \bullet \text{H} \bullet \text{H} \bullet \text{H} \bullet \text{C} \bullet \\
\text{H} \\
\text{H} \cdot \text{C} \cdot \text{H} \\
\text{H}
\end{array}
\]

Done!
LDS Mechanics (cont.)

- An example: \( \text{Cl}_2\text{O} \)

\[
\begin{array}{c}
\text{Cl} \quad \text{O} \quad \text{Cl} \\
\text{Cl} \quad \text{O} \quad \text{Cl}
\end{array}
\]

\[
\begin{align*}
20 \text{ e}^- \\
- 4 \text{ e}^- & \quad (\text{bonding}) \\
16 \text{ e}^- \\
- 12 \text{ e}^- & \quad (\text{lone, Cl}) \\
4 \text{ e}^- \\
- 4 \text{ e}^- & \quad (\text{lone, O}) \\
0 \text{ e}^- 
\end{align*}
\]
Multiple bonds

Sometimes atoms have to share more than one pair of electrons in order to fulfill the octet rule, like $\text{O}_2$.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O:O} & \\
\text{O=O} &
\end{align*}
\]
• An example: CO$_2$

\[
\begin{align*}
\text{O} & \cdot \text{O} \cdot \text{C} \\
\text{O} & \cdot \text{C} \cdot \text{O}
\end{align*}
\]

\[
\begin{align*}
16 \text{ e}^- & - 4 \text{ e}^- \text{ (bonding)} \\
12 \text{ e}^- & - 12 \text{ e}^- \text{ (lone, O)} \\
0 \text{ e}^- &
\end{align*}
\]
LDS Rules of Thumb

1. In a polyatomic molecule, the atom that can make the most number of bonds typically goes in the center.
   
   - This atom is also typically the least electronegative atom in the molecule.

2. H can only form one bond, so it goes on the outside of the molecule...H is a terminal atom.

3. If O and H both appear in a chemical formula, they are probably bonded to each other.

4. When several C atoms appear in the same formula, they are probably bonded to each other in a chain.
   
   - In other situations the C atoms can form a closed loop, or branching structures, but we will not consider such cases here.
Same Atoms, Different LDSs

• We have assumed up to this point that there is one correct Lewis structure for a given chemical formula.

• There are systems for which more than one Lewis structure is possible:
  – **Resonance Structures**: Same atomic linkages, different bonding (single vs. double, etc). Real structure is an “average” of the available resonance structures.
  – **Structural Isomers**: Different atomic linkages. “Formal Charge” is used to determine most likely structure.
Resonance Structures

• The classic example: $O_3$.

Both structures are correct!
Resonance Structures (cont.)

• In this example, O₃ has two resonance structures:

\[
\begin{align*}
\text{O} = \text{O} - \text{O} & \quad \leftrightarrow \quad \text{O} - \text{O} = \text{O} \\
\end{align*}
\]

• Conceptually, we think of the bonding as an average of these two structures.

• Electrons are delocalized between the oxygens such that on average the bond strength is equivalent to 1.5 O-O bonds.

Bond lengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>148</td>
</tr>
<tr>
<td>O=O</td>
<td>121</td>
</tr>
<tr>
<td>Ozone</td>
<td>128</td>
</tr>
</tbody>
</table>
Resonance structures of nitrate ion:

The three N-O bonds on $\text{NO}_3^-$ are equivalent.

They each exhibit intermediate bonding character between single and double bonds.
Example

• Draw all the resonance structures for $\text{N}_3^{-}$.

\[3(5 \text{ e}^{-}) + 1 \text{ e}^{-} = 16 \text{ e}^{-}\]
Structural Isomers

• Different sets of atomic linkages can be used to construct correct LDSs. Consider Cl₂O:

[Diagrams of Cl–O–Cl and Cl–Cl–O]

• Both are correct, but is one of them “more” correct?
• Define “Formal Charge”...the apparent charge on the atoms in a LDS when atoms have not contributed equal numbers of electrons to the bonds joining them.

• **Formal Charge** is a shorthand way to describe how homogeneously electron density is distributed in a molecule.

• When comparing structural isomers, the structure with the most homogeneous distribution of electron density – minimal FC on all atoms – tends to be more correct (but the only way to really know is to do an experiment!)
Formal Charge

- Example: CO₂

\[
\begin{array}{c}
O = C = O \\
\text{e}^- & -6 & -4 & -6 \\
Z^+ & +6 & +4 & +6 \\
\text{FC} & 0 & 0 & 0 \\
\end{array}
\quad
\begin{array}{c}
O = O = C \\
-6 & -4 & -6 \\
+6 & +6 & +4 \\
0 & +2 & -2 \\
\end{array}
\quad
\begin{array}{c}
O - O \equiv C \\
-7 & -4 & -5 \\
+6 & +6 & +4 \\
-1 & +2 & -1 \\
\end{array}
\]

More Correct
Triatomic Bonding Patterns

Compare CO$_2$ with N$_3^-$...both 16 e$^-$ systems:

\begin{align*}
\text{N} & \equiv \text{N} \equiv \text{N} \\
\text{N} & \equiv \text{N} \equiv \text{N} \\
\text{N} & \equiv \text{N} \equiv \text{N}
\end{align*}

Most correct structure has two double bonds.

Also note: the sum of the FCs equals the overall charge on the species.
What is the most likely structure of N$_2$O?

The LDS rules are just guidelines... they give you a first approximation to molecular structure.

To know the real answer you have to do experiments!
Formal Charge Guidelines

• Both electrons in a lone pair belong to the atom in question.

• Bonding electrons are split evenly between the bonded atoms.

• The sum of the FCs for all the atoms in a molecule or ion must equal the overall charge on the species.

• If nonequivalent LDSs exist for a molecule, the LDS with the FCs closest to zero and any negative charges on electronegative atoms *tends* to best describe the species.
  
  – *To know the real answer you must conduct experimental studies of bond length, bond energy, etc...*
Beyond the Octet Rule

• There are numerous exceptions to the octet rule.
• We’ll deal with the following classes of violation:
  – Sub-octet systems (less than 8 electrons)
  – Valence shell expansion (more than 8 electrons)
  – Radicals (odd number of electrons)
Sub-Octet Systems

- Some atoms (for example, Be, B, and Al) can form quasi-stable molecules that do not fulfill the octet rule.

- Experiments demonstrate that the B-F bond strength is consistent with single bonds only.
Sub-Octet Systems (cont.)

• Sub-octet molecules will react with other molecules so that their octet becomes satisfied.
• The octet rule is satisfied by the reacting partner providing an electron pair.
• A bond in which both electrons come from one of the atoms is called a *coordinate covalent bond*.
Valence Shell Expansion

• For third-row elements ("Period 3"), the energetic proximity of the d orbitals allows for the participation of these orbitals in bonding.

• When this occurs, more than 8 electrons can surround a third-row element.

• Example: ClF₃ (a 28 e⁻ system)

F obeys octet rule

Cl is breakin’ the law!
It has 10 electrons.
Valence Shell Expansion (cont.)

• Typical atoms that demonstrate valence-shell expansion are P, S, and larger halogens (Cl, Br, and I).

• Example: $\text{PCl}_5$
  
  30 e$^-$

Here, Cl obeys octet rule.
P exhibits valence expansion with its 10 electrons.
Valence Shell Expansion (cont.)

Lewis-dot structure & valence shell expansion:

- As before, assign electrons to bonds and lone pairs to give each atom an octet.
- Assign any remaining electrons to elements with accessible d orbitals.
- Formal charge is used to discriminate between multiple LDSs.
- When it is necessary to exceed the octet for one of several third-row or higher) atoms, put extra electrons on the central atom.
- **DO NOT expand an octet unless it's absolutely necessary.**

Example: $I_3^- \quad 22 \text{ e}^-$

Satisfying the octet for each atom uses up 20 electrons

Formal charge: $FC = 0 \quad -1 \quad 0 \quad -2 \quad +1 \quad 0$
Valence Shell Expansion (cont.)

- Bonding in molecules containing noble-gas atoms involves valence shell expansion
- Example: Determine the structure of $\text{XeO}_3$

26 e$^-$

\[ \text{O}--\text{Xe}^{+3}--\text{O} \quad \text{O}--\text{Xe}^{+2}--\text{O} \]

\[ \text{O}--\text{Xe}^{+1}--\text{O} \quad \text{O}--\text{Xe}^{0}--\text{O} \]
Based on formal charge, which structure for IO₄⁻ is most likely?

A

B

C

D
Radicals: Odd-Electron Systems

• Finally, one can encounter odd electron systems where full pairs will not exist.

• Example: Chlorine Dioxide. $19\, \text{e}^-$

\[
\text{O} - \text{Cl} - \text{O} \quad \text{Unpaired electron}
\]
Radicals: Odd-Electron Systems

• Strategy: Generally attempt to put the odd electron on the central atom. However, the LDS rules were not intended to be applied to odd-electron systems.

• Example: NO₂.  17 e⁻

N is suboctet; therefore NO₂ is likely to be highly reactive.
LDS Summary

- C, N, O, and F almost always obey the octet rule.
- B, Be, and Al are often sub-octet.
- Second row (Period 2) elements never exceed the octet rule.
- Third Row (Period 3) elements and beyond can use valence shell expansion to exceed the octet rule.
- Formal charge can often help indicate the most likely structure among a set of resonance structures.
- When writing an LDS, first satisfy the octet for all atoms. If electrons remain, place them on atoms that have d-orbitals.
- If there is an odd number of electrons, try to place the single electron on the least electronegative atom.
- An LDS is a best guess. The real structure can only be determined experimentally!!

- Writing correct Lewis structures is a trial-and-error process. You have to practice...a lot!
The Length and Strength of Bonds

**Bond Energy**: energy required to break a particular bond in the gas phase.

- **always positive** since breaking a bond always requires energy
- a quantitative measure of a bond’s strength (i.e. the potential energy of molecule)
- The higher the bond energy → the stronger the bond.

- Breaking a bond always requires energy while forming a bond always releases energy.
Bond energies are always defined in terms of the energy required to break the bond.

If a bond forms, energy is released.
Exothermic Reaction

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

DH is a **state function**: it only describes the difference in enthalpy between the initial and final **states** of the system.

DH does not contain any information about the physical pathway from reactants to products.

In 162, you will study chemical kinetics, which attempts to quantify **how** reactions occur and the **activation energies** involved.
**Endothermic Reaction**

\[ \text{heat} + \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO(} \text{g}) \]

Net absorption of energy as heat!
Enthalpy change of the formation of a bond is equal in magnitude but opposite in sign to the bond energy:

\[ \Delta H_{\text{bond forming}} = -\Delta H_{\text{bond breaking}} \]

Heat of Rxn is given by:

\[ \Delta H_{\text{rxn}} = \sum \Delta H_{\text{bond breaking}} + \sum \Delta H_{\text{bond forming}} \]
<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (pm)</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>154</td>
<td>348</td>
</tr>
<tr>
<td>C—C</td>
<td>134</td>
<td>614</td>
</tr>
<tr>
<td>C≡C</td>
<td>120</td>
<td>839</td>
</tr>
<tr>
<td>C—N</td>
<td>143</td>
<td>293</td>
</tr>
<tr>
<td>C≡N</td>
<td>138</td>
<td>615</td>
</tr>
<tr>
<td>C≡N</td>
<td>116</td>
<td>891</td>
</tr>
<tr>
<td>C—O</td>
<td>143</td>
<td>358</td>
</tr>
<tr>
<td>C≡O</td>
<td>123</td>
<td>843(^a)</td>
</tr>
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<td>1072</td>
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<td>C—H</td>
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<td>607</td>
</tr>
<tr>
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<tr>
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</tr>
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</tr>
<tr>
<td>S—O</td>
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<td>265</td>
</tr>
<tr>
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<td>143</td>
<td>523</td>
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<tr>
<td>S—S</td>
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<td>266</td>
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<tr>
<td>S—H</td>
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<td>347</td>
</tr>
<tr>
<td>H—H</td>
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<tr>
<td>H—F</td>
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<td>H—I</td>
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<td>Cl—Cl</td>
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<td>243</td>
</tr>
<tr>
<td>Br—Br</td>
<td>228</td>
<td>193</td>
</tr>
<tr>
<td>I—I</td>
<td>266</td>
<td>151</td>
</tr>
</tbody>
</table>

\(^a\)The bond energy of the C≡O bond in CO₂ is 799 kJ/mol.

\[ \text{Oxygen: } 121 \text{ pm} \]

\[ \text{Ozone: } 128 \text{ pm} \]

\[ \text{Hydrogen peroxide: } 148 \text{ pm} \]
Bond Length

Bond length decreases as the bond order (number of bonds) increases.

Bond strength increases as bond length decreases.
Example

\[ \Delta H_{\text{rxn}} = \sum \Delta H_{\text{bond breaking}} + \sum \Delta H_{\text{bond forming}} \]

- Use bond enthalpies to determine the heat of reaction for the formation of hydrogen fluoride gas from its elements:

\[ \text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2 \text{HF}(\text{g}) \]

**Bonds Broken:**

\[ \text{H} - \text{H} \quad \Delta H_{\text{break H-H}} = +432 \text{ kJ/mol} \]
\[ \text{F} - \text{F} \quad \Delta H_{\text{break F-F}} = +154 \text{ kJ/mol} \]

**Bonds Formed:**

\[ 2 \times \text{H} - \text{F} \quad \Delta H_{\text{form H-F}} = -\Delta H_{\text{break H-F}} = -565 \text{ kJ/mol} \]

\[ \Delta H_{\text{rxn}} = \Delta H_{\text{break H-H}} + \Delta H_{\text{break F-F}} + 2 \cdot \Delta H_{\text{form H-F}} \]
\[ = (+432 \text{ kJ/mol}) + (+154 \text{ kJ/mol}) + 2 \cdot (-565 \text{ kJ/mol}) \]

\[ \Delta H_{\text{rxn}} = -544 \text{ kJ/mol} \]

Compare to experiment:

\[ \Delta H_{\text{rxn}}^{\text{exp}} = -542 \text{ kJ/mol} \]

\[ \text{That's pretty good!!} \]
However...

• In general, there is no advantage to using bond enthalpies rather than enthalpies of formation to determine reaction enthalpies.

• Enthalpies of formation are typically known to high precision, whereas bond enthalpies are only average values.

• Furthermore, bond enthalpies are tabulated for isolated molecules in the gaseous state...they cannot be applied to molecules in close contact in liquid or solid states.
  – Why not??

• But bond enthalpies can be useful in determining whether an unfamiliar reaction is endo- or exothermic.
Example

\[ \Delta H_{\text{rxn}} = \sum \Delta H_{\text{bond breaking}} + \sum \Delta H_{\text{bond forming}} \]

One naturally-occurring reaction involved in the sequence of reactions leading to the destruction of ozone is:

\[ \text{NO}_2(g) + \text{O}(g) \rightarrow \text{O}_2(g) + \text{NO}(g) \]

Is this reaction predicted to be endo- or exothermic?

**Bonds Broken:**
- \( \text{N} - \text{O} \)
  \[ \Delta H_{\text{break N} - \text{O}} = +222 \text{ kJ/mol} \]
- \( \text{N} = \text{O} \)
  \[ \Delta H_{\text{break N}=\text{O}} = +607 \text{ kJ/mol} \]

**Bonds Formed:**
- \( \text{O} = \text{O} \)
  \[ \Delta H_{\text{form O}=\text{O}} = -\Delta H_{\text{break O}=\text{O}} = -498 \text{ kJ/mol} \]
- \( \text{N} \equiv \text{O} \)
  \[ \Delta H_{\text{form N}=\text{O}} = -\Delta H_{\text{break N}=\text{O}} = -607 \text{ kJ/mol} \]

\[ \Delta H_{\text{rxn}} = \Delta H_{\text{break N} - \text{O}} + \Delta H_{\text{break N}=\text{O}} + \Delta H_{\text{form O}=\text{O}} + \Delta H_{\text{form N} = \text{O}} \]

\[ = (+222 \text{ kJ/mol}) + (+607 \text{ kJ/mol}) + (-498 \text{ kJ/mol}) + (-607 \text{ kJ/mol}) \]

\[ \Delta H_{\text{rxn}} = -276 \text{ kJ/mol} \]

This reaction is predicted to be exothermic.