Announcements

- Lab week change
  Due to Chancellor's Inauguration Week activities, classes on the afternoon of April 26 are cancelled, so we have to move the lab that day to one week earlier. Since we are having Exam 3 on April 27, it makes sense to move all the labs that week to one week earlier.
  Summary: Lab 9 will happen the week of April 17 (this week!). There will be no labs the week of April 24. This is a shift to one week earlier for everyone.

- Exam #3 is next Thursday, April 27
  - Practice exam and key are also now posted.

- The final exam is scheduled for Monday, May 15, 8:00-11:00am
  It will NOT be in our regularly scheduled lecture hall (S-1-006). The final exam location has been changed to Snowden Auditorium (W-1-088).
More announcements

Information you need for registering for the second semester of general chemistry

- If you will take it in the summer:
  - Look for chem 104 in the summer schedule (includes lecture and lab)

- If you will take it in the fall:
  - Look for chem 116 (lecture) and chem 118 (lab). These courses are co-requisites.

- If you plan to re-take chem 103, in the summer it will be listed as chem 103 (lecture + lab). In the fall it will be listed as chem 115 (lecture) + chem 117 (lab), which are co-requisites.
  - Note: you are only eligible for a lab exemption if you previously passed the course.

Agenda

- The gray area between ionic and molecular and why compounds can’t always be clearly categorized as ionic or molecular
- The Lewis structure model for predicting bonding arrangements in molecular compounds
- The electronegativity model for predicting bond polarity
Map of Chapter 8

- What holds ions together
  - Predicting qualitative trends
- What holds molecules together
  - Predicting enthalpy of reaction from bond energies
- Ionic vs. covalent character of bonds: polarity and electronegativity model
- Lewis structure model
  - Simple structures (octet rule), with single and multiple bonds
  - Resonance structures
  - More complicated structures (breaking the octet rule)
  - Formal charges
- Bond strength and length
  - Using Lewis structures to predict
  - Using Hess’s law and bond enthalpies

Reminder: Electron Affinity

Electron affinity measures how much an atom “likes” electrons

Except not the noble gases
Building Lewis Structures

1. Determine central atom (atom with lowest electron affinity because electron density will spread as far as possible, given the opportunity)
2. Count total number of valence electrons in molecule
3. Arrange atoms around central atom
4. Start with single bonds
5. Place remaining valence electrons
6. Move electrons to form octets, making double or triple bonds where necessary

Check: Make sure you have conservation of electrons

Practicing the Steps

Draw the Lewis structure for ammonium (NH$_4^+$)

1. N is central because H atoms can only bond once
2. Total valence electrons
   - 5 on N
   - 1 on each H gives 4 more
   - Ion has +1 charge, meaning one electron is removed
   - Total = 5 + 4 – 1 = 8

The rest of the steps:
Practicing the Steps

Draw the Lewis structure for the nitrate ion (NO$_3^-$)

1. N is central because it has the least electron affinity
2. Total valence electrons
   - 5 on N
   - 6 on each of three O atoms gives 18 more
   - Ion has -1 charge, meaning one electron is added
   - Total = 5 + 18 + 1 = 24

The rest of the steps:

![Lewis structure of NO$_3^-$](image)

Try building these structures:

1) NO$_2^+$
2) CN$^-$
3) SCN$^-$
4) O$_3$

Isoelectronic = same number of (valence) electrons and same number of atoms to distribute them around

Which two of the above structures are isoelectronic?

What is true about isoelectronic species?
Resonance Structures

- What do these structures have in common?
- How are they different?
- Which of these is the actual structure of NO₃⁻?

Note: This is not a correct Lewis structure. It is drawn this way only to emphasize the bond order.

Other examples of resonance

S-O bond order =

C-O bond order =

C-C bond order =
Bond Order and Bond Length/Strength

- **Bond order**
  - Single bond is bond order 1
  - Double bond is bond order 2
  - Triple bond is bond order 3

- **Bond strength**
  - The greater the bond order, the stronger the bond (the more energy required to break the bond)

- **Bond length**
  - The greater the bond order, the shorter the bond length

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**TABLE 8.4 Average Bond Enthalpies (kJ/mol)**

<table>
<thead>
<tr>
<th>Single Bonds</th>
<th>C––H 413</th>
<th>N––H 391</th>
<th>O––H 463</th>
<th>F––F 155</th>
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<tbody>
<tr>
<td>C––C</td>
<td>348</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C––N</td>
<td>293</td>
<td>N––O 201</td>
<td>O––F 190</td>
<td>Cl––F 253</td>
</tr>
<tr>
<td>C––O</td>
<td>358</td>
<td>N––F 272</td>
<td>O––Cl 203</td>
<td>Cl––Cl 242</td>
</tr>
<tr>
<td>C––F</td>
<td>485</td>
<td>N––Cl 200</td>
<td>O––I 234</td>
<td></td>
</tr>
<tr>
<td>C––Cl</td>
<td>328</td>
<td>N––Br 243</td>
<td>Br––F 237</td>
<td></td>
</tr>
<tr>
<td>C––Br</td>
<td>276</td>
<td>H––H 436</td>
<td>S––H 339</td>
<td>Br––Cl 218</td>
</tr>
<tr>
<td>C––I</td>
<td>240</td>
<td>H––F 567</td>
<td>S––Cl 253</td>
<td>Br––Br 193</td>
</tr>
<tr>
<td>C––S</td>
<td>259</td>
<td>H––Cl 431</td>
<td>S––Br 218</td>
<td></td>
</tr>
<tr>
<td>Si––H</td>
<td>323</td>
<td>H––Br 366</td>
<td>S––S 266</td>
<td>I––Cl 208</td>
</tr>
<tr>
<td>Si––Si</td>
<td>226</td>
<td>H––I 299</td>
<td></td>
<td>I––Br 175</td>
</tr>
<tr>
<td>Si––Cl</td>
<td>301</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si––O</td>
<td>368</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si––Cl</td>
<td>464</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Multiple Bonds</th>
<th>C––C 614</th>
<th>N––N 418</th>
<th>O2 495</th>
</tr>
</thead>
<tbody>
<tr>
<td>C––C</td>
<td>839</td>
<td>N––N 941</td>
<td></td>
</tr>
<tr>
<td>C––N</td>
<td>615</td>
<td>N––O 607</td>
<td>S––O 523</td>
</tr>
<tr>
<td>C––N</td>
<td>891</td>
<td></td>
<td>S––S 418</td>
</tr>
<tr>
<td>C––O</td>
<td>799</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C––O</td>
<td>1072</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Bond length

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (Å)</th>
<th>Bond</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>1.54</td>
<td>N≡N</td>
<td>1.47</td>
</tr>
<tr>
<td>C≡C</td>
<td>1.34</td>
<td>N≡N</td>
<td>1.24</td>
</tr>
<tr>
<td>C≡C</td>
<td>1.20</td>
<td>N≡N</td>
<td>1.10</td>
</tr>
<tr>
<td>C—N</td>
<td>1.43</td>
<td>N—O</td>
<td>1.36</td>
</tr>
<tr>
<td>C≡N</td>
<td>1.38</td>
<td>N—O</td>
<td>1.22</td>
</tr>
<tr>
<td>C≡N</td>
<td>1.16</td>
<td>O—O</td>
<td>1.48</td>
</tr>
<tr>
<td>C—O</td>
<td>1.43</td>
<td>O—O</td>
<td>1.21</td>
</tr>
<tr>
<td>C≡O</td>
<td>1.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡O</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Formal Charges

A comparison between the valence electrons originally contributed by an atom and the electrons that it looks like the atom would have if all bonds were broken and electrons reassigned democratically.

The valence electrons that were originally contributed:
- each O had 6
- the N had 5

Electrons assigned democratically if bonds hypothetically broken

Therefore, the formal charges on each atom are

Notice that the sum of the formal charges must equal the ion charge
Formal Charges and Alternative Structures

- If more than one Lewis structure exists, the most stable structure is the one in which the formal charges make most sense
  - Negative formal charges on atoms with large electron affinity
  - Positive formal charges on atoms with small ionization energies (small electron affinity)

Which is the most stable structure?

A Range of Bond Types

Bond “types” are not separable into a true dichotomy between covalent and ionic. Instead there is a range of covalent character vs. ionic character of bonds.

Increasing ionic character of bond
Increasing “bond polarity”

- Nonpolar covalent: Perfectly covalently shared electrons
- Polar covalent: Bonding electrons exhibit greater electron density (δ-) on one atom in the bond than on the other (δ+)
- Ionic: Ions with full charges (unshared electrons)
Electronegativity Model to Explain Bond Polarity

- Definition: the attraction that a given atom has for the electrons that are in a bond
- Early idea related to electron affinity (energy required to add an electron to an atom) and ionization energy (energy required to remove an electron from an atom)
- Linus Pauling invented an electronegativity scale of elements based on comparing bond energies of elements bonded to themselves and to other elements

Pauling attributed additional bond strength in HF to extra Coulomb attraction due to partial ionic character of HF bond compared to equal sharing of electrons in H₂ and F₂. Maximum "electronegativity" at F set to 4.0.

**Pauling’s Electronegativity Scale**

*Electronegativity measures the ability of an atom to attract electrons to itself*
Predicting Bond Polarity
Using Electronegativities

- Electronegativity is a measure of the ability of an atom to attract electrons to itself
- Bond polarity depends on the difference between the electronegativities of the two elements that are in a bond

Increasing bond polarity

Predicting Bond Polarity

- Electronegativity measures ability of an atom to attract electrons to itself
- Bond polarity depends on the difference between the electronegativities of the two elements that are in a bond

Increasing ionic character of bond
Increasing “bond polarity”

Nonpolar covalent
- Perfectly covalently shared electrons

Polar covalent
- Bonding electrons exhibit greater electron density (δ-) on one atom in the bond than on the other (δ+)

Ionic
- Ions with full charges (unshared electrons)
Electronegativities Allow You to Compare Bond Polarity

- Which bond is most polar? Which bond is least polar?
- Which end of the bond is the negative pole (greater electron density)? Which end is the positive pole (less electron density)?

The bond between C and N in CN⁻

Is less polar than

The bond between C and O in H₂CO

Is less polar than

The bond between C and F in CH₃F

Comparing a series

Use the information above to explain why the dipole moments of this series of hydrogen halides exhibits the following behavior:

Dipole moments are HF = 1.82 D, HCl = 1.08 D, HBr = 0.82 D, HI = 0.44 D

Note: “D” stands for Debyes, the S.I. units in which dipole moment is measured in the laboratory.
Exceptions to Octet Rule

1. Less than an octet on an atom
   - Only happens with Group 3A elements (such as boron) because these elements have 3 valence electrons so they make 3 bonds (not 4)
   - Examples: BF₃, B(OH)₃

2. Odd number of electrons
   - Impossible for all electrons to be paired
   - Lone electron usually resides on atom with lowest electron affinity (which is usually central atom)
   - Called “free radicals”
   - Very reactive because electrons are more stable in pairs
   - Examples: NO (11 valence electrons), NO₂ (17 valence electrons)

3. More than an octet on an atom
   - This is what we will spend the rest of the semester studying

Examples of more than an octet on the central atom

Only elements in periods 3 and higher (e.g., S, Cl) can do this.
Using bond enthalpies to predict enthalpy change during a reaction

- Breaking bonds costs energy
- When bonds form, energy is released (bonded atoms are more stable)

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

**Example**

*Exercise on p. 332*

Estimate \( \Delta H \) for the reaction

\[ \text{H—N—N—H(g) } \rightarrow \text{ N≡N(g) } + \text{ 2 H—H(g)} \]

Bonds to break (endothermic):
- four N-H bonds @ 391 kJ/mol
- one N-N bond @ 163 kJ/mol

Bonds to form (exothermic):
- one N≡N bond @ 941 kJ/mol
- two H-H bonds @ 436 kJ/mol

\[ \text{Energy input } = \quad \text{Energy released } = \]

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

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