Chapter 13: Phenomena

Scientists measured the bond angles of some common molecules. In the pictures below each line represents a bond that contains 2 electrons. If multiple lines are drawn together these are double or triple bonds and contain 4 and 6 electrons respectively. What patterns do you notice from the data?

- a) Bond Angles: 107°
- b) Bond Angles: 109.5°
- c) Bond Angles: 109.5°
- d) Bond Angles: 105°
- e) Bond Angles: 120°
- f) Bond Angles: 119°
- g) Bond Angles: 180°
- h) Bond Angles: 180°
- i) Bond Angles: 180°
- j) Bond Angles: 180°

Chapter 13: Bonding: General Concepts

**Types of Bonding**

- **Ionic Bonds**: Formed when a lower energy can be achieved by the complete transfer of one or more electrons from the atoms of one element to those of another; the compound is then held together by electrostatic attraction between the ions.

- **Covalent Bonds**: Formed when the lowest energy structure can be achieved by sharing electrons.

**What ions do atoms form?**

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration (Atom)</th>
<th>Gain/Lose Electrons</th>
<th>Ion Formed</th>
<th>Electron Configuration (Ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Shapes of Molecules (VSEPR)**

**Big Idea**: Bonds are formed from the attraction between oppositely charged ions or by sharing electrons. Only the valence electrons participate in bonding.

- **Ionic Solids**: Assembly of cations and anions stacked together in a regular array. Ionic solids are composed of charged particles which attract each other due to their opposite charge. The overall charge on an ionic solid is neutral.

- **Ionic Compounds**: Are represented with formula units (lowest ratio of types of atoms in the compound).

**Covalent Compounds**: Are represented with formula units (lowest ratio of types of atoms in the compound).

**Notes**: In general, atoms gain or lose electrons until they have the same number of electrons as the nearest noble gas.
Chapter 13: Bonding: General Concepts

Types of Bonding

Steps to calculate the energy needed to form an ionic bond:

Step 1: Standard states to gaseous single atom state
- Na(s) \rightarrow Na(g) 97 \text{kJ/mol}
- \frac{1}{2}F_2(g) \rightarrow F(g) 80.9 \text{kJ/mol}

Step 2: Both atoms have to form ions
- Na(g) \rightarrow Na^+(g) + e^-(g) 494 \text{kJ/mol} (ionization energy)
- F(g) + e^-(g) \rightarrow F^-(g) -323 \text{kJ/mol} (-)electron affinity

Step 3: The ions need to come together to form a crystal (Lattice Energy)
- Na^+(g) + F^-(g) \rightarrow NaF(s) -923 \text{kJ/mol}

Total Reaction:
- Na(s) + \frac{1}{2}F_2(g) \rightarrow NaF(s)
- \Delta H = 97 + 80.9 + 494 + 323 + 923 = -575 \text{kJ/mol}

Note: When energy is released, the sign is negative because no work is needed to make the reaction happen.

Types of Bonding

- Once neighboring ions come into contact they start to repel each other.
- \text{E}_p \propto e^{-d^2/d^*}
- \text{d}^* \text{ is a constant that is commonly taken to be 34.5 pm}

The potential energy of an ionic solid is a combination of the favorable Coulombic interaction of the ions and the unfavorable exponential increase which results when the atoms touch. The ideal bond length occurs at the minimum potential energy.

Energy Minimum Occurs: \text{E}_{p,\text{min}} = \frac{-z_1z_2e^2}{4\pi\varepsilon_0}\left(1 - \frac{1}{d^*}\right)^2

Note: \text{d}^* is a constant that is commonly taken to be 34.5 pm

Types of Bonding

- Coulombic Potential Energy
  \text{E}_{\text{Coulomb}} = \frac{z_1z_2e^2}{4\pi\varepsilon_0d}

The total potential energy is the sum of all the potential energies

\text{E}_p = \frac{z_1z_2e^2}{4\pi\varepsilon_0d} + \text{Lattice Energy}

Note: \text{L} = 1 - \frac{1}{d^*}

\text{E}_p = -2n^2\text{e}^2/4\pi\varepsilon_0d

Types of Bonding

- Covalent Bond: A pair of electrons shared between two atoms (occurs between two non metals)

Note: In covalent bond formation, atoms go as far as possible toward completing their octets by sharing electron pairs.

Electronegativity

- Electronegativity (\chi): The ability of an atom to attract electrons to itself when it is part of a compound

Note: The atom with higher electronegativity has a stronger attractive power on electrons and pulls the electrons away from the atom with the lower electronegativity.

<table>
<thead>
<tr>
<th>Difference in Electronegativity</th>
<th>Type of Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1.8</td>
<td>Mostly Ionic</td>
</tr>
<tr>
<td>0.4-1.8</td>
<td>Polar Covalent</td>
</tr>
<tr>
<td>&lt; 0.4</td>
<td>Mostly Covalent</td>
</tr>
<tr>
<td>0</td>
<td>Non-polar Covalent</td>
</tr>
</tbody>
</table>

The dividing line between ionic and covalent bonds is hazy.
Chapter 13: Bonding: General Concepts

Electronegativity

What makes covalent bonds partly ionic?
- Electric Dipole: A positive charge next to an equal but opposite negative charge.

40 Dipole moment
- Electric Dipole Moment ($\mu$): The magnitude of the electric dipole [units debye ($D$)].

**Note:** The dipole moment associated with H-Cl is about 1.1 $D$.

- Polar Covalent Bond: A covalent bond between atoms that have partial electric charges.

Electric Dipole:

Lewis Structures

- Lewis Symbols: The chemical symbol of an element, with a dot for each valence electron.

Step 1: Determine the number of valence $e^-$ from electron configuration.
Step 2: Place 1 dot around the element for each valence electron.

General Rules (Covalent Lewis Structures)
- All valence electrons of the atoms in the Lewis structures must be shown.
- Generally, electrons are paired. Except for odd electron molecules such as NO and NO$_2$.
- Generally, each atom has 8 electrons in its valence shell with the exception of H which only needs 2 valence electrons.
- Multiple bonds (double and triple bonds) can be formed.

- Show atoms by their chemical symbols (ex. H)
- Show covalent bonds by lines (ex. F–F)
- Show lone pairs of electrons by pairs of dots (ex. :)

Electronegativity

- What makes ionic bonds partly covalent?
- Polarizability ($\alpha$): The ease with which the electron cloud of a molecule can be distorted.

As the cation’s positive charge pulls on the anion’s negative electrons, the spherical electron cloud of the anion becomes distorted in the direction of the cation. This causes the bond to have covalent bond properties.

- Polar Covalent Bond: A covalent bond between atoms that have partial electric charges.

Polarizability ($\alpha$): The ease with which the electron cloud of a molecule can be distorted.

Distorted electron cloud

Polarizable anion

Note: The larger the anion the easier it is to distort the electron cloud.

Step 1: Determine the electron configuration of the elements in the compound.
Step 2: Determine the electron configuration of the ions that the elements form.
Step 3: Draw the Lewis symbols for the ions. Do not forget to include charge. The cations should have no electrons around them and the anions should have 8 electrons around them.
Step 4: Organize the Lewis symbols such that cations are next to anions.

Drawing Ionic Lewis Structures

- Step 1: Determine the number of valence electrons on each atom; for ions adjust the number of electrons to account for the charge.
- Step 2: Calculate the number of electrons that are needed to fill each atom’s octet (or duplet, in the case of H).
- Step 3: Calculate the number of bonds:
  \[ \text{# Bonds} = \frac{\text{Wanted } e^– (\text{Step 2}) - \text{Valence } e^– (\text{Step 1})}{2} \]
- Step 4: Calculate the number of electrons left over: \[ \# e^– = \text{Valence } e^– - 2 (\# \text{Bonds}) \]
- Step 5: Place bonds/electrons around elements so that octets/duplets are satisfied.

Drawing Covalent Lewis Structures (for structures that obey octet rule)
- Step 1: Count the number of valence electrons on each atom; for ions adjust the number of electrons to account for the charge.
- Step 2: Calculate the number of electrons that are needed to fill each atom’s octet (or duplet, in the case of H).
- Step 3: Calculate the number of bonds:
  \[ \text{# Bonds} = \frac{\text{Wanted } e^– (\text{Step 2}) - \text{Valence } e^– (\text{Step 1})}{2} \]
- Step 4: Calculate the number of electrons left over: \[ \# e^– = \text{Valence } e^– - 2 (\# \text{Bonds}) \]
- Step 5: Place bonds/electrons around elements so that octets/duplets are satisfied.
Tips When Drawing Lewis Structures

- **How to pick central atom:**
  - Choose the central atom to be the atom with the lowest ionization energy (atom closest to the lowest left hand corner of the periodic table)
  - Arrange the atoms symmetrically around the central atom

**Examples:**
SO₂ would be arranged OSO not SOO

**Note:** Acids are an exception to the rule because H is written first in acids.

**Note:** In simple formulas the central atom is often written first, followed by the atoms attached to it.

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**Formal Charge:**

The electric charge of an atom in a molecule assigned on the assumption that the bonding is nonpolar covalent.

Formal Charge = Valence e⁻ − e⁻ Surrounding Atom

**Note:** The formal charge on neutral molecules must add up to zero.

**Note:** The formal charge on ions must add up to the charge on the ion.

Generally, compounds with the lowest formal charges possible (charges closest to 0) are favored.

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**Resonance:** A blend of Lewis structures into a single composite hybrid structure.

**Resonance Hybrid:** The composite structure that results from a resonance.

**Delocalized Electrons:** Electrons that are spread over several atoms in a molecule.

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**What is the Lewis Structure for SCN⁻?**

\[
\begin{align*}
\text{Valence e}^- & = 1(6) + 1(4) + 1(5) + 1 = 16 \\
\text{Wanted e}^- & = 1(8) + 1(8) + 1(8) + 24 = 40 \\
\# \text{ bonds} & = \frac{(\text{wanted } e^-) - (\text{valence } e^-)}{2} = \frac{40 - 16}{2} = 12 \\
\# e^- & = (\text{valence } e^-) - 2(\# \text{ bonds}) = 16 - 2(12) = 8 \\
\end{align*}
\]

Which structure is most likely?

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**What is the Lewis Structure for PO₄^{3⁻}?**

\[
\begin{align*}
\text{Valence e}^- & = 1(5) + 4(6) + 1(3) + 32 = 40 \\
\text{Wanted e}^- & = 1(8) + 4(8) = 40 \\
\# \text{ bonds} & = \frac{(\text{wanted } e^-) - (\text{valence } e^-)}{2} = \frac{40 - 32}{2} = 4 \\
\# e^- & = (\text{valence } e^-) - 2(\# \text{ bonds}) = 40 - 2(4) = 32 \\
\end{align*}
\]
Lewis Structures

- When the central atom in a molecule has empty d-orbitals, it may be able to accommodate 10, 12, or even more electrons, this is referred to as an expanded valence shell.
  
  **Note:** This only applies to nonmetal atoms in Period 3 and later

- Size also plays a role in how many atoms can fit around a given molecule.
  
  **Example:**
  
  PCl₅ Known to exist
  NCl₅ Not known to exist (N is too small for the to fit 5 Cl atoms around it)
  
  **Note:** On homework problems only expand octets if there is no other way to accommodate electrons or if the problem tells you to minimize the formal charge.

Strength/Length of Covalent Bonds

- **Dissociation Energy (D):** The energy required to separate bonded atoms

<table>
<thead>
<tr>
<th>Avg. Bond Energies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
</tr>
<tr>
<td>H-F</td>
</tr>
<tr>
<td>H-Cl</td>
</tr>
<tr>
<td>C-H</td>
</tr>
<tr>
<td>C-C</td>
</tr>
<tr>
<td>C-N</td>
</tr>
<tr>
<td>C-O</td>
</tr>
<tr>
<td>N-H</td>
</tr>
<tr>
<td>N=N</td>
</tr>
<tr>
<td>( \text{N}=\text{O} )</td>
</tr>
</tbody>
</table>

- **Strength/Length of Covalent Bonds**

  - Double bonds are not twice as strong as a single bond.
  - Triple bonds are not three times as strong as a single bond.

- **Student Question (ADDITION)**

  Single bonds are __________ triple bonds.
  
  a) longer than
  b) shorter than
  c) the same length as

- **Strength/Length of Covalent Bonds**

  Which of the following has the longest carbon-oxygen bond?
  
  Hint: You must draw the Lewis structures.

  a) CO
  b) CO₂
  c) \( \text{CO}_2^+ \)
  d) CH₃OH

**Take Away From Chapter 13**

- **Big Idea:** Bonds are formed from the attraction between oppositely charged ions or by sharing electrons. Only the valence electrons participate in bonding. The shape of the molecules maximize the distance between areas of high electron density.

- **Types of Bonding**

  - **Ionic Bonds (metal/non metal)**
    - Be able to write electron configuration of ions. (26, 27, 29, 30)
    - Be able to predict size of ions. (23, 24, 25)
    - Be able to predict formula unit ionic compound. (33)
  
  - **Covalent Bonds (non metal/non metal)**

**Chapter 13: Bonding: General Concepts**
Take Away From Chapter 13

- **Electronegativity**
  - Know the general electronegativity trend. (15)
  - Know that covalent bonds can have ionic because of dipole moments.
  - Be able to identify the most polar bond. (16, 18, 19)
  - Know that ionic bonds can have covalent character because of polarizability.

- **Lewis Structures**
  - Be able to draw Lewis symbols (atoms).
  - Be able to draw Lewis structures of ionic compounds.
  - Be able to draw Lewis structures of covalent compounds. (57, 58)
  - Know how to calculate formal charges. (78, 79)
  - Identification of most likely Lewis structure.
  - Know when multiple resonance structures are possible for a compound. (40, 61, 65, 73)
  - Know when atoms can expand their octets (group 3 and greater). (80)

Take Away From Chapter 13

- **Strength/Length of Covalent Bonds**
  - Know how to calculate $\Delta H$ from bond dissociation energies.
    \[ \Delta H = \Sigma H_{\text{formed}} - \Sigma H_{\text{broken}} \]
  - Know how to estimate the length of bonds.
    - Triple < Double < Single (74)