CHAPTER 7: COVALENT BONDING

- You should understand the nature of the covalent bond.
- You should be able to draw the Lewis electron-dot structure for any atom, molecule, or polyatomic ion.
- When a single Lewis structure does not adequately reflect the properties of a substance, you should be able to draw resonance forms for it.
- You should be able to calculate the formal charge on an atom in an electron-dot structure.
- You should be able to give examples of substances that violate the octet rule, either because they are electron-deficient or because they have expanded octets.
- You should be able to apply the principles of VSEPR theory to identify the geometry of any molecule or ion.
- You should be able to identify the orbital hybridization of the central atom in a molecule or polyatomic ion.
- You should be able to identify the sigma and pi bonds in an electron-dot structure.

7.1 LEWIS STRUCTURES; THE OCTET RULE

Noble gases are generally nonreactive because they have a full valence shell. Many atoms form monatomic ions by either losing electrons or gaining electrons, in order to achieve the electron configuration of a noble gas. Gilbert Lewis suggested that nonmetal atoms can acquire a noble gas configuration by sharing electrons to form a covalent bond.

\[
\begin{align*}
\text{H} & \quad 1s^1 \\
\text{F} & \quad 1s^2 2s^2 2p^5 \\
\text{H}_2\text{F}_2 & \quad 1s^2 1s^2 2s^2 2p^6 
\end{align*}
\]

The Lewis electron dot structures below indicate the valence electrons for elements in Groups 1-2 and Groups 13-18.

In a Lewis electron dot structure, the electrons normally exist in pairs. Bonding pairs are covalent bonds. Nonbonding pairs are lone pairs, or unshared pairs.

A single bond consists of one bonding pair. A double bond consists of two bonding pairs. A triple bond consists of three bonding pairs.

All other things being equal, triple bonds are shorter than double bonds, which are shorter than single bonds.

\[
\text{C–C} \quad > \quad \text{C=O} \quad > \quad \text{C≡C}
\]
The bond energy is the energy required to break a bond. This value increases as you go from single bonds to double bonds to triple bonds.

\[
\begin{align*}
\text{C–C} & \quad < \quad \text{C=\text{C}} \quad < \quad \text{C\equiv\text{C}} \\
\text{weakest bond} & \quad \text{lowest bond energy} \quad \text{strongest bond} \quad \text{highest bond energy}
\end{align*}
\]

The octet rule states that nonmetal atoms tend to achieve a noble gas configuration by being surrounded by eight electrons. Hydrogen atoms could be said to obey the "duet rule," since they are normally surrounded by two electrons.

The following rules are helpful for writing the Lewis structure for a molecule or polyatomic ion:

1. Calculate the total number of valence electrons by adding up the valence electrons for each atom in the chemical formula. If you have an ion, then you need to
   (a) add a certain number of electrons based on the negative charge, or
   (b) subtract a certain number of electrons based on the positive charge

2. Draw a skeleton structure for the species, joining atoms by single bonds. The central atom is normally the atom that has the lowest electronegativity value. It is often the element that is written first in the chemical formula. The terminal atoms tend to be hydrogen, oxygen, or the halogens.


4. If there are electrons available, add them to the terminal atoms to complete their octets.

5. Any atom (besides hydrogen, beryllium, boron, or aluminum) that still does not have enough electrons to complete its octet will probably need to form a double or triple bond. Move electrons from lone pairs on the terminal atoms to form double or triple bonds. Atoms that tend to form multiple bonds are C, N, P, O, and S. Hydrogen and halogens do NOT form double bonds.

Certain molecules like sulfur dioxide have an interesting bonding situation. One Lewis structure does not adequately describe the properties of the molecule. If SO\textsubscript{2} contains one S-O bond and one S=O bond, the bond lengths would be different. However, experiments show that the two S-O bond lengths are the same.

The bonding situation in SO\textsubscript{2} is described through resonance structures, which are separated by a double headed arrow. Resonance structures are used whenever a single Lewis structure does not adequately reflect the properties of a substance. The actual bond length in SO\textsubscript{2} would be somewhere between the length of an S-O single bond and an S=O double bond.

The bond order is obtained by averaging the bonds over all the possible resonance structures. In the case of SO\textsubscript{2}, we calculate the bond order as follows. \( (2 + 1) \) divided by 2, which is equal to 1.5. The bond order of the S-O bond in SO\textsubscript{2} is equal to 1.5.

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

The following molecules (or ions) can be described with resonance structures: O\textsubscript{3}, NO\textsubscript{2}\textsuperscript{−}, NO\textsubscript{4}\textsuperscript{−}, CO\textsubscript{3}\textsuperscript{2−}, and benzene (C\textsubscript{6}H\textsubscript{6}). Resonance structures are NOT two different structures that shift back and forth in equilibrium. The true structure of the molecule or ion is intermediate between those of the resonance forms. The electrons are said to be delocalized over the entire atom group. Resonance structures differ only in the distribution of electrons, NOT in the arrangement of atoms.
In this example of **structural isomers**, each molecule has the same molecular formula (C₂H₆O), but there is a difference in the connections between the atoms.

These are two different structural isomers of C₂H₆O

Consider these two Lewis electron dot structures for CH₄O.

Both structures satisfy the octet rule. However, only one of them is more likely to occur. You can apply the concept of **formal charge** to determine which structure seems more plausible.

Formal charge = (# of valence electrons in the free atom) – (# of electrons “assigned” to the atom)

“Assigning” electrons to an atom in a Lewis dot structure is based on the following rules:
- Each covalent bond counts as 1 electron (1/2 the bond)
- Each lone pair of electrons on an atom counts as 2 electrons

In the structure on the left,
- each H has a formal charge of 0
- the C has a formal charge of 0
- the O has a formal charge of 0

In the structure on the right,
- each H has a formal charge of 0
- the C has a formal charge of -1
- the O has a formal charge of +1

If you are trying to decide which Lewis structure more likely, you should try to pick the one that
- keeps the formal charges as close to zero as possible
- puts negative charges on the atoms that have the largest electronegativity values

Using these guidelines, the structure on the **left** is preferred.

Analyze these three Lewis dot structures for the cyanate ion. Assign formal charges to each atom in each structure. Which Lewis dot structure do you think is most favorable, based on formal charges?

Do not confuse formal charges with oxidation states! Formal charges are assigned to specific Lewis dot structures based on the bonds and the lone pairs. Oxidation numbers are “pseudo-charges” assigned to atoms in a given formula and these have nothing to do with the Lewis electron dot structure. Oxidation numbers are assigned based on the differences in electronegativity between the atoms.

For example, in the Lewis structure for CO₂, each atom has a formal charge of zero.

But the oxidation number of each oxygen is -2,

and the oxidation number of the carbon is +4.
Exceptions to the Octet Rule

Examples of substances with incomplete octets: \( \text{BeX}_2, \text{BX}_3, \) and \( \text{AlX}_3 \) where \( X = \text{halogen} \)

Examples of substances with an odd number of electrons: \( \text{NO, NO}_2, \text{ClO}_2, \) and \( \text{O}_2^- \)

Substances with an odd number of electrons are often called free radicals. They are very reactive. For example, \( \text{NO}_2 \) would likely form a bond with itself, to produce the dimer \( \text{N}_2\text{O}_4 \).

Examples of substances with more than eight electrons around the central atom: \( \text{PX}_5, \text{SX}_6, \text{ClX}_3, \text{XeF}_4 \)

Atoms that tend to expand their octets include the following:

<table>
<thead>
<tr>
<th>Group 15</th>
<th>Group 16</th>
<th>Group 17</th>
<th>Group 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd period</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>4th period</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>5th period</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
</tbody>
</table>

How can an atom expand its octet? If an atom has an empty d orbital, it can use these orbitals for bonding. The extra pairs of electrons in the expanded octets utilize some of the d-orbitals. Atoms like C, N, and O do not form expanded octets because they do not have a d orbital available in the 2\(^{\text{nd}}\) principal energy level (\( n = 2 \)).

7.2 MOLECULAR GEOMETRY

The geometry of a Lewis dot structure can be determined by applying the principles of Valence Shell Electron Pair Repulsion (VSEPR) Theory. In the VSEPR model, the orbitals containing electron pairs from covalent bonds and nonbonding pairs are oriented in three-dimensional space so as to be as far apart as possible.

In the following examples, \( A \) is the central atom, and \( X \) is a terminal atom. There are NO unshared pairs on the central atom.

<table>
<thead>
<tr>
<th>Species Type</th>
<th>Orientation of electron pairs</th>
<th>Predicted Bond Angles</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX(_2)</td>
<td>Linear</td>
<td>180°</td>
<td>( \text{BeF}_2, \text{CO}_2, \text{HCN}, \text{N}_2\text{O}_2, \text{N}_3^- )</td>
</tr>
<tr>
<td>AX(_3)</td>
<td>Trigonal Planar</td>
<td>120°</td>
<td>( \text{BF}_3, \text{SO}_3, \text{NO}_3^-, \text{CO}_3^{2-} )</td>
</tr>
<tr>
<td>AX(_4)</td>
<td>Tetrahedral</td>
<td>109.5°</td>
<td>( \text{CF}_4, \text{NH}_4^+, \text{ClO}_4^-, \text{SO}_4^{2-}, \text{PO}_4^{3-} )</td>
</tr>
<tr>
<td>AX(_5)</td>
<td>Trigonal Bipyramidal</td>
<td>90°, 120°, 180°</td>
<td>( \text{PF}_5, \text{AsF}_5, \text{SF}_5^+ )</td>
</tr>
<tr>
<td>AX(_6)</td>
<td>Octahedral</td>
<td>90°, 180°</td>
<td>( \text{SF}_6, \text{SeF}_6, \text{PF}_6^- )</td>
</tr>
</tbody>
</table>
Many molecules and polyatomic ions contain at least one unshared pair of electrons on the central atom. The VSEPR model can be used to predict the geometry of such structures. The geometry of the resulting structure is described by the atoms that are bonded to the central atom. The lone pairs influence the shape, but are not included in the molecular geometry.

In the NH₃ molecule, the central atom has one lone pair and three atoms around it. It would have the designation AX₃E. The four electron clouds are arranged with tetrahedral geometry. One of the corners of the tetrahedron is occupied by a lone pair. The NH₃ molecule has a shape that is determined by the atoms. The shape is trigonal pyramidal.

The bond angles here are around 107°, which is a little smaller than the predicted angle of 109.5°. This is because lone pairs repel a little more and take up a little more space compared to bonding pairs.

In the H₂O molecule, the central atom has two lone pairs and two atoms around it. It would have the designation AX₂E₂. The four electron clouds are arranged with tetrahedral geometry. Two of the corners of the tetrahedron are occupied by lone pairs. The H₂O molecule has a shape that is determined by the atoms. The shape is bent.

The bond angle is around 105°, which is a little smaller than the predicted angle of 109.5°. This is again because lone pairs repel a little more and take up a little more space compared to bonding pairs.

<table>
<thead>
<tr>
<th>Species Type</th>
<th>Orientation of electron pairs</th>
<th>Predicted Bond Angles</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX₂</td>
<td>Linear</td>
<td>180°</td>
<td>BeF₂, CO₂, N₂O, N₃⁻</td>
</tr>
<tr>
<td>AX₃</td>
<td>Trigonal Planar</td>
<td>120°</td>
<td>BF₃, SO₃, NO₃⁻, CO₃⁻²</td>
</tr>
<tr>
<td>AX₂E</td>
<td>Bent</td>
<td>&lt; 120°</td>
<td>O₃, SO₂, NO₂⁻</td>
</tr>
<tr>
<td>AX₄</td>
<td>Tetrahedral</td>
<td>109.5°</td>
<td>CF₄, ClO₄⁻, SO₄⁻², PO₄⁻³</td>
</tr>
<tr>
<td>AX₃E</td>
<td>Trigonal Pyramidal</td>
<td>&lt; 109.5°</td>
<td>NH₃, PCl₃, AsF₃</td>
</tr>
<tr>
<td>AX₂E₂</td>
<td>Bent</td>
<td>&lt; 109.5°</td>
<td>H₂O, OF₂, ClO₂⁻</td>
</tr>
<tr>
<td>AX₅</td>
<td>Trigonal Bipyramidal</td>
<td>90°, 120°, 180°</td>
<td>PF₅, AsF₅, SF₅⁺</td>
</tr>
<tr>
<td>AX₄E</td>
<td>See-Saw</td>
<td>90°, 120°, 180°</td>
<td>SF₄, SeF₄</td>
</tr>
<tr>
<td>AX₃E₂</td>
<td>T-shaped</td>
<td>90°, 180°</td>
<td>ClF₃</td>
</tr>
<tr>
<td>AX₂X₃</td>
<td>Linear</td>
<td>180°</td>
<td>XeF₂, Br₃⁻</td>
</tr>
<tr>
<td>AX₆</td>
<td>Octahedral</td>
<td>90°, 180°</td>
<td>SF₆, SeF₆, PF₆⁻</td>
</tr>
<tr>
<td>AX₅E</td>
<td>Square Pyramidal</td>
<td>90°, 180°</td>
<td>ClF₅</td>
</tr>
<tr>
<td>AX₄E₂</td>
<td>Square Planar</td>
<td>90°, 180°</td>
<td>XeF₄</td>
</tr>
</tbody>
</table>
A covalent bond may be classified as polar or nonpolar. Polar bonds are formed when two atoms have different values for electronegativity. Generally speaking, an EN difference of around 0.4 – 2.0 would be considered polar. A nonpolar bond is formed when the two atoms have very similar EN values.

Polar covalent bonds are characterized by unequal sharing of the bonding electrons. A dipole is formed in which there is a partial positive charge on the atom that is more electropositive and a partial negative charge on the atom that is more electronegative. Consider H-F as an example. The electron cloud is more concentrated around the F atom.

A polar molecule is one that has a positive and negative pole. The extent of the polarity is called the dipole moment. A nonpolar molecule such as H₂ has a dipole moment of zero.

For diatomic molecules, determining the polarity is easy. For molecules with three or more atoms, the geometry must be considered, as well as the polarity of the bonds. Here are some examples:

The molecules on the left are nonpolar because their bond dipoles all cancel each other out.

The molecules on the right are polar because their bond dipoles do NOT cancel each other out.

*If the polar A-X bonds in a molecule AXₘEₙ are arranged symmetrically around the central atom A, then the molecule is nonpolar.*

Molecules of the type AX₂ (linear), AX₃ (triangular planar), and AX₄ (tetrahedral) are nonpolar. Examples include CO₂, BF₃, and CCl₄.

Molecules of the type AX₂E (bent), AX₂E₂ (bent), and AX₃E (triangular pyramidal) are polar. Examples include SO₂, H₂O, and NH₃.
Consider the electron configuration of fluorine. How many covalent bonds should an atom of fluorine form?

F

\[ \begin{array}{c}
\uparrow \\
1s\\
\downarrow \\
2s\\
\uparrow \\
2p_x\\
\downarrow \\
2p_y\\
\uparrow \\
2p_z\\
\downarrow \\
3s
\end{array} \]

It has one unpaired electron. It needs an additional electron to fill out its outer energy level. That extra electron could come from another fluorine atom or a hydrogen atom, for example.

Now look at the electron configuration of nitrogen. How many covalent bonds should an atom of nitrogen form?

N

\[ \begin{array}{c}
\uparrow \downarrow \\
1s\\
\uparrow \downarrow \\
2s\\
\uparrow \downarrow \\
2p_x\\
\uparrow \downarrow \\
2p_y\\
\uparrow \downarrow \\
2p_z\\
\downarrow \\
3s
\end{array} \]

It has three unpaired electrons. It needs three additional electrons to fill out its outer energy level. Those extra electrons could come from another nitrogen atom, or from three hydrogen atoms, for example.

From these two examples, one might assume that the number of covalent bonds that are formed by an atom will always be equal to the number of unpaired electrons in the atom’s electron configuration.

How many covalent bonds does an atom of beryllium form? What about boron? What about carbon?

Be

\[ \begin{array}{c}
\uparrow \downarrow \\
1s\\
\uparrow \downarrow \\
2s\\
\uparrow \downarrow \\
2p_x\\
\uparrow \downarrow \\
2p_y\\
\uparrow \downarrow \\
2p_z\\
\downarrow \\
3s
\end{array} \]

B

\[ \begin{array}{c}
\uparrow \downarrow \\
1s\\
\uparrow \downarrow \\
2s\\
\uparrow \downarrow \\
2p_x\\
\uparrow \downarrow \\
2p_y\\
\uparrow \downarrow \\
2p_z\\
\downarrow \\
3s
\end{array} \]

C

\[ \begin{array}{c}
\uparrow \downarrow \\
1s\\
\uparrow \downarrow \\
2s\\
\uparrow \downarrow \\
2p_x\\
\uparrow \downarrow \\
2p_y\\
\uparrow \downarrow \\
2p_z\\
\downarrow \\
3s
\end{array} \]

Clearly, predictions of bonding that are based on the number of unpaired electrons will not work.

We need a new picture for explaining the way that an atom forms covalent bonds. This involves hybrid orbitals.

When beryllium forms bonds with its two valence electrons, the atomic orbitals of the beryllium atom will change. The 2s orbital is mixed or hybridized with the 2p orbital to form two new \textit{sp hybrid orbitals}.

Similar arguments can be made for explaining boron and carbon.

Boron forms three covalent bonds by forming three \textit{sp\textsuperscript{2} hybrid orbitals}. (one s + two p)

Carbon forms four covalent bonds by forming four \textit{sp\textsuperscript{3} hybrid orbitals}. (one s + three p)

Hybrid orbitals can be used for both bonding pairs of electrons as well as nonbonding electron pairs.
Recall that some molecules like PCl$_5$ and SCl$_6$ can have expanded octets.

In these examples, the extra electron pairs in an expanded octet will occupy d orbitals.

Phosphorus can form five covalent bonds by forming five sp$^3$d hybrid orbitals. (one s + three p + one d)
Sulfur can form six covalent bonds by forming six sp$^3$d$^2$ hybrid orbitals. (one s + three p + two d)

The number of hybrid orbitals formed is equal to the number of orbitals that are mixed together.

<table>
<thead>
<tr>
<th>Species Type</th>
<th># of Atoms Bonded to Central Atom</th>
<th># of Lone Pairs around Central Atom</th>
<th>Hybridization of Central Atom</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX$_2$</td>
<td>2</td>
<td>0</td>
<td>sp</td>
<td>Linear</td>
<td>BeF$_2$, CO$_2$, N$_2$O, N$_3^-$</td>
</tr>
<tr>
<td>AX$_3$</td>
<td>3</td>
<td>0</td>
<td>sp$^2$</td>
<td>Trigonal Planar</td>
<td>BF$_3$, SO$_3$, NO$_3^-$, CO$_3^{2-}$</td>
</tr>
<tr>
<td>AX$_2$E</td>
<td>2</td>
<td>1</td>
<td>sp$^2$</td>
<td>Bent</td>
<td>O$_3$, SO$_2$, NO$_2^-$</td>
</tr>
<tr>
<td>AX$_4$</td>
<td>4</td>
<td>0</td>
<td>sp$^3$</td>
<td>Tetrahedral</td>
<td>CF$_4$, ClO$_4^-$, SO$_4^{2-}$, PO$_4^{3-}$</td>
</tr>
<tr>
<td>AX$_3$E</td>
<td>3</td>
<td>1</td>
<td>sp$^3$</td>
<td>Trigonal Pyramidal</td>
<td>NH$_3$, PCl$_3$, AsF$_3$</td>
</tr>
<tr>
<td>AX$_2$E$_2$</td>
<td>2</td>
<td>2</td>
<td>sp$^3$</td>
<td>Bent</td>
<td>H$_2$O, OF$_2$, ClO$_2^-$</td>
</tr>
<tr>
<td>AX$_5$</td>
<td>5</td>
<td>0</td>
<td>sp$^3$d</td>
<td>Trigonal Bipyramidal</td>
<td>PF$_5$, AsF$_5$, SF$_5^+$</td>
</tr>
<tr>
<td>AX$_4$E</td>
<td>4</td>
<td>1</td>
<td>sp$^3$d</td>
<td>See-Saw</td>
<td>SF$_4$, SeF$_4$</td>
</tr>
<tr>
<td>AX$_3$E$_2$</td>
<td>3</td>
<td>2</td>
<td>sp$^3$d</td>
<td>T-shaped</td>
<td>ClF$_3$</td>
</tr>
<tr>
<td>AX$_2$X$_3$</td>
<td>2</td>
<td>3</td>
<td>sp$^3$d</td>
<td>Linear</td>
<td>XeF$_2$, Br$_3^-$</td>
</tr>
<tr>
<td>AX$_6$</td>
<td>6</td>
<td>0</td>
<td>sp$^3$d$^2$</td>
<td>Octahedral</td>
<td>SF$_6$, SeF$_6$, PF$_6^-$</td>
</tr>
<tr>
<td>AX$_5$E</td>
<td>5</td>
<td>1</td>
<td>sp$^3$d$^2$</td>
<td>Square Pyramidal</td>
<td>ClF$_5$</td>
</tr>
<tr>
<td>AX$_4$E$_2$</td>
<td>4</td>
<td>2</td>
<td>sp$^3$d$^2$</td>
<td>Square Planar</td>
<td>XeF$_4$</td>
</tr>
</tbody>
</table>
Consider the Lewis dot structures of ethene (C₂H₄) and ethyne (C₂H₂):

In ethene, each carbon atom has sp² hybridization.

In ethyne, each carbon atom has sp hybridization.

The extra electrons that are used to make the double bond and the triple bond are NOT located in hybrid orbitals.

These extra electron pairs that are involved in the double bond and the triple bond have no effect on the overall geometry of the molecule.

So where are these extra electrons located? The electrons used to make double and triple bonds are located in pi (π) orbitals.

There are two types of bonding orbitals. There are sigma (σ) orbitals, and there are pi (π) orbitals.

The sigma (σ) bond consists of an electron pair that is located in the region between the two bonded atoms.

The pi (π) bond consists of an electron pair that is located in the lobes above and below the bond axis.

In general, to find the number of sigma (σ) and pi (π) bonds, remember that

- All single bonds are sigma (σ) bonds.
- One of the electron pairs in a multiple bond is a sigma (σ) bond; the other electron pairs are pi (π) bonds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th># of sigma (σ) bonds</th>
<th># of pi (π) bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>C₂H₆</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>ethene</td>
<td>C₂H₄</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>ethyne</td>
<td>C₂H₂</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

![Ethane](image1.png) ![Ethylene](image2.png) ![Acetylene](image3.png)