

Chapter 9 - The Chemical Bond

As we begin this chapter you should take a moment to review “The History of the Development of the Period Table” that we discussed at the beginning of our study of Chapter 4. (Remember that most of our discussion was not in the book!)

Similarities between the chemical and physical properties of the elements were known early in the nineteenth century. We mentioned Doebereiner (“triads”), Newlands (“Law of Octaves”), Mendeleev and Meyer, and Moseley (protons, “atomic number” to arrange the elements).

Section 9-1: Bond Formation and Representative Elements

Some atoms combine with other elements to form compounds. Some of the noble gases do not form compounds. Why the elements do or do not form compounds provides a clue to understanding the bonding of the representative elements.

1) Sec 9-1.1 - The Octet Rule

In Chapter 2 we were introduced to the idea of ionic compounds and molecular compounds. We learned that these involved ionic bonds (those between ions with opposite charges) and covalent bonds (electrons shared between atoms in molecules). The strength of these bonds is measured by the energy it takes to break the bonds and this is called **bond energy**.

We continued this discussion in Chapter 4 when we began thinking about the interactions of elements to form compounds and saw how the atoms came together to make both ionic and molecular compounds that we named.

a) Chemical Bonding by Transferring Electrons

We have studied many instances of metals and non-metals reacting by forming cations (metals) and anions (non-metals). These compounds are held together by the charges on the ions involved - ionic bonds.

b) Chemical Bonding by Electron Sharing

Many compounds are not made of ions. The nonionic compounds consist of atoms bonded tightly together in the form of molecules. The bonds holding the atoms together form when pairs of electrons are shared between atoms. Such bonds are called covalent bonds. Electron pairs are shared, and a covalent bond forms between two atoms when both atoms are nonmetals (including hydrogen).

c) Nature of the Covalent Bond

A covalent bond consists of a pair of electrons of opposite spin filling an atomic orbital on both of the bonded atoms. At any instant the two electrons being shared may be located at any of various points around the two nuclei. There is, however, a greater probability of finding the two electrons

In Chapter 8 we talked about the trends within the Periodic Table - specifically the trend in atomic size and the trend in ionization energy. These remain important but the more useful trend for this chapter is the trend in the **electronegativity**.

When different atoms react, a bond can form in which electrons are shared - either equally or unequally. How electrons are shared can be described by a property called electronegativity: **the relative ability of an atom to attract one or more electrons to itself**. In the book, we will talk specifically about this in Section 9-7.

However, there is an over-arching relationship that describes the bonding (either ionic or covalent) in the representative elements. The stability of the noble gas configuration influences the number of electrons that atoms tend to lose or acquire by either transferring or sharing. All the noble gases (except for helium) have filled outer *s* and *p* sublevels. This is a total of eight electrons and referred to as an *octet* of electrons.

The bonding we will talk about in this chapter is dictated by the **octet rule**, which states that *atoms will gain or lose or share electrons to get to a stable eight outer electrons*. It should be noted that helium is a partial exception in that it only has a filled 1*s* shell containing two electrons. Therefore, it has a stable configuration with only its two electrons, compared to the other noble gases.

One can also use the electron configurations to determine the number of electrons gained or lost in forming ions. For most of our discussions we will not talk about the transition and inner transition elements. These have their own considerations.

5) Sec 9-1.2 - Valence Electrons and Dot Symbols

The outer *s* and *p* electrons in the atoms of a representative element are referred to as the **valence electrons**. Only these electrons are involved in bonding, so we will focus on them. In 1916 **Lewis dot symbols** or **structures** (named after the American chemist Gilbert Lewis, 1875 - 1946) were developed to represent valence electrons as dots around the symbol of the element.

1	2	13	14	15	16	17	18
H·							He:
Li·	·Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
Na·	·Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·
K·	·Ca·				·Se·	·Br·	·Kr·
Rb·	·Sr·				·Te·	·I·	·Xe·
Cs·	·Ba·						

6) Lewis Structures

In 1916 an American chemist Gilbert N. Lewis developed a method to use to describe valence electrons in atoms. He was trying to explain the information becoming available as Bohr and others were finding out more about electron. This method involves using dots around the atomic symbol to show the valence electrons. The rules for writing **Lewis structures** (also known as **Lewis dot structures** or **electron dot structures**) are

based on observations of many compounds from which chemists have learned that *the most important requirement for the formation of a stable compound is that the atoms achieve noble gas configurations (by gaining, losing, or sharing electrons).*

The representative metals in Groups 1, 2 and 13 lose electrons to achieve an electron configuration that is like that of the previous noble gas. (Think: noble gas abbreviations.)

The representative non-metals in Groups 15, 16 and 17 gain electrons to get to the next higher noble gas. In both cases, the ion charge depends upon the number of electrons either lost or gained to get the noble gas electronic configuration.

Atoms (usually non-metals) share electrons with other atoms to get to the noble gas configuration.

Note, again, that the octet rule gets modified for the elements H, Li, and Be since their noble gas is helium which only has its two electrons. Sometimes this is referred to as the “duet rule”.

Section 9-2: Formation of Ions and Ionic Compounds

We will see how the octet rule gets us to the same results for the charges on ions that we discovered by the position of elements on the Periodic Table.

7) Sec 9-2.1 - Formation of Binary Ionic Compounds

In Chapter 4 we formed binary ionic compounds by balancing the charges of the ions - the net charge for the compound had to be neutral.

Lewis structures can be used to help explain the formation of ions and how these either lose or gain electrons to get to noble gas configurations. The representative metals lose their valence electrons (“dots”) to get to an octet. However many electrons or dots the metal loses is the charge on the cation.

The non-metals fill their valence electrons or dot structure to get to the octet. (How many holes or spaces are around the non-metal?) The number of electrons or dots the non-metals add is the charge on the anion.

Most often, Lewis structures are used for molecules with covalent bonds in the first, second and third periods. Since all of the noble gases (with the exception of helium which has 2 valence electrons) have eight valence level electrons, the number of electrons needed about each atom in a covalent bond (with the exception of hydrogen) is **eight** (the octet rule). Hydrogen only needs **two** (helium configuration, sometimes called a *duet rule*).

The explanation we used in Chapter 4 for being able to balance charges in NaCl, Na₂O, and Al₂O₃ also work with the dots structures and coming up with formulas from them.

8) Ionic Bonding and Structures of Ionic Compounds

When metals and non-metals react, electrons are transferred. The structure of the

compounds has much to do with how these cations and anions can pack around each other. To understand the packing of ions it helps to realize that **a cation is always smaller than the parent atom and an anion is always larger than the parent atom.** Figure 8-19 and the image in your Chapter 8 Notes show some examples of the changes in sizes as cations and anions are formed.

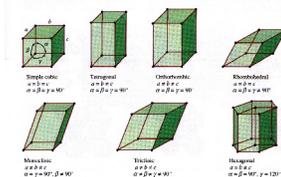
This packing of ions is also true with the polyatomic ions from Table 4-2. A difference is that the atoms within the polyatomic ions are held together by covalent bonds. We will explain these shortly. However, packing is affected by size.

9) Sec 9-2.2 - Other Representative Element Ions

For some of the higher atomic number representative metals, the expected ions are formed but also some others (as shown on the Periodic Table). There are explanations for how these are formed but they all form ions in patterns that one might expect although they do not follow the octet rule.

10) Sec 9-2.3 - The Physical States of Ionic Compounds

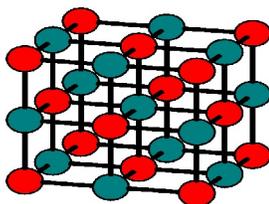
Remember that ionic compounds do not exist in distinct molecular units with a cation attached to an anion. With NaCl, for example, one Na^+ and then each Cl^- is surrounded continue and form a three-dimensional structure that is called a **lattice**.



compounds do not exist in cation attached to an anion. It is surrounded by several Cl^- ions; by a number of Na^+ ions. These dimensional structure that is

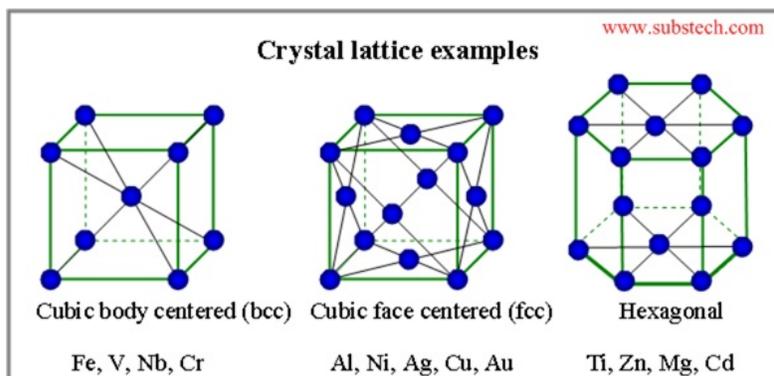
The lattice is held together by the strong electromagnetic interactions of the opposite charges of the ions.

A drawing representing with the chloride anions



the sodium cations interspersed in a crystal of rock salt.

These are some of the more common (although not all) lattice structures for ionic compounds:



13) Sec 9-3.3 - The Electrons in Polyatomic Ions

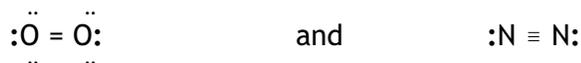
Like molecular compounds, the atoms in polyatomic ions share electrons in covalent bonds. Take for example the hypochlorite ion, ClO^{-1} . Remember that the -1 tells us that we have one more electron than the atoms themselves or one more electron than the total valence electrons.

$$\begin{array}{r} \text{from a Cl atom} = 7 \\ \text{from an O atom} = 6 \\ \hline \text{from the charge} = 1 \\ \hline \text{total electrons} = 14 \end{array}$$

Two atoms bonded together with 14 electrons has a structure similar to F_2 , which also has a total of 14 electrons.

14) Sec 9-3.4 - Double and Triple Bonds

So far we have discussed examples of two atoms sharing two electrons. There are also occasions when two or three pairs of electrons are shared between two atoms. The sharing of two pairs of electrons is known as a **double bond**. The sharing of three pairs is a **triple bond**. The double bond is indicated as =, and the triple bond as \equiv .

Section 9-4: Writing Lewis Structures

The octet rule is the key to writing the correct Lewis structures for many molecules and polyatomic ions. Later on we will see that we can also use the Lewis structure to help us predict the geometry of simple (and not-so-simple) molecules.

15) Sec 9-4.1 - Rules for Writing Lewis Structures for Molecules

We want to develop procedures for writing Lewis structures for molecules. Remember that Lewis structures only involve the valence electrons on atoms (the **outer s** and **p** electrons).

The best way to get a correct Lewis structure for molecules is to follow a systematic approach. If we consistently work through the steps, we will always be on the correct path. My steps are slightly different from those in the book. Take your pick, but know what you are doing and be consistent!

Step 1: Count up the total number of valence electrons from all the atoms. We do not worry where the electrons come from. The important thing is the **total**.

Step 2: Pick a central atom. The other atoms will be positioned around this atom. Certain atoms can never be the central atom, but most often it will be the first atom listed in a formula. Usually the formula will give us hints as to how things are placed. "Draw a silly picture" - "DSP" - indicating the placements or a skeletal structure.

- Step 3:** Place two electrons in each bond between each pair of bonded atoms. (That is, if there is a bond it has to be at least a single bond, and so indicate this.)
- Step 4:** Place the remaining electrons on the ATTACHED atoms to fulfill the octet rule (or the duet rule for hydrogen; that is, once the bond is formed for hydrogen it does not need any more electrons).
- Step 5:** If there are electrons still remaining, place them on the central atom to fulfill the octet rule for it.
- Step 6:** If the central atom does not have an octet, form double bonds by bringing pairs of electrons from one of the attached atoms. If necessary, form triple bonds. (However, H, F, Cl, Br, and I can only form single bonds when they are attached atoms.)
- Single bonds share 2 electrons.
Double bonds share 4 electrons.
Triple bonds share 6 electrons.

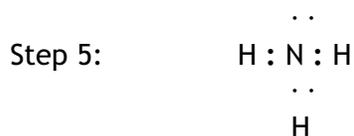
Remember: With this procedure we do not care where the electrons come from. We are merely counting the total and distributing them about the atoms so that each atom fulfills the octet rule.

Example: The Lewis structure for the water molecule, H_2O .

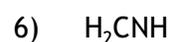
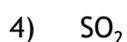
- Step 1: $1 + 1 + 6 = 8$ total valence electrons
- Step 2: H O H
- Step 3: H : O : H
- Step 4: Since the attached atoms are hydrogens, they cannot accept any more electrons (duet rule).
- Step 5: $\begin{array}{c} \cdot \cdot \\ \text{H} : \text{O} : \text{H} \\ \cdot \cdot \end{array}$

Example: The Lewis structure of the ammonia molecule, NH_3 .

- Step 1: $1 + 1 + 1 + 5 = 8$ total valence electrons
- Step 2: H N H
 H
- Step 3: H : N : H
 $\cdot \cdot$
 H
- Step 4: Since the attached atoms are hydrogens, they cannot accept any more electrons.



Examples - Give Lewis Structures for each of the following:



16) Sec 9-4.2 - Exceptions to the Octet Rule

The octet rule works much of the time. However, as in the case with H_2 it does not work all the time. There are other ways to explain some of the behaviors of molecules.

Such molecules as NO_2 , BF_3 , and PCl_5 have structures that are not in line with the octet rule.

Section 9-5: Resonance Structures

17) Determining and Drawing Resonance Structures

Sometimes we can write more than one **valid** Lewis structure for a molecule. When this occurs, we say that the molecule has **resonance** and we can draw **resonance structures**; that is, all the valid Lewis structures for the molecule. Sometimes we draw a structure that attempts to represent the various structures in one and we can call this a **resonance hybrid**.

Example: There are three resonance structures for the molecule carbon dioxide, CO_2 .

Example: There are three resonance structures for the carbonate ion, CO_3^{-2} .

Example: Write the resonance structures for ozone, O_3 , where one of the oxygens is in the center.

In summary: Sometimes we need double or triple bonds to satisfy the octet rule. Writing Lewis structures, like balancing equations, is a trial-and-error process. Always start with single bonds and add multiple bonds as needed.

This procedure works 99% of the time. There are, however, some exceptions that fall into the other 1% of molecules as mentioned before. Two examples of these are NO_2 (17 valence electrons) and BF_3 (an electron deficient molecule).

18) A Summary of Some Other Factors with Lewis Structures

- a) A coordinate covalent bond is formed when one atom contributes both bonding electrons in a covalent bond. (ex.: ammonium ion)
- b) Resonance - Resonance structures occur when two or more valid electron dot formulas can be written for a molecule. (ex.: carbon dioxide - 3 forms; ozone - 2 forms)
- c) Sometimes it is impossible to write electron dot structures that fulfill the octet rule. This happens whenever the total number of valence electrons in the species is an odd number. (ex.: NO_2 with 17 electrons, one is always unpaired)
- d) Molecular Orbitals - When two atoms combine, their atomic orbitals overlap to produce molecular orbitals. Two atomic orbitals combine to make two molecular orbitals even though only one bond is formed. One of these is a bonding orbital which is a molecular orbital whose energy is lower than that of the atomic orbitals from which it is formed. The other is an antibonding orbital which is a molecular orbital whose energy is higher than that of the atomic orbitals from which it is formed.

A sigma bond is formed when two atomic orbitals combine to form a molecular orbital that is symmetrical along the axis connecting the two nuclei.

In a pi bond, the electrons are most likely to be found in sausage-shaped regions above and below the bond axis of the bonded atoms.

Section 9-6: Formal Charge

Formal charge is a way to further explain structures that do not always seem to satisfy the octet rule.

19) Sec 9-6.1 - Resonance Structures that Violate the Octet Rule

Formal charge is the charge that each atom would have if the electrons in the bonds were divided equally between the two atoms. Formal charge is another way to describe what seems to be the difference between the Lewis structure and the way the molecule seems to behave chemically.

Two notable atoms that contribute to this are S and P.

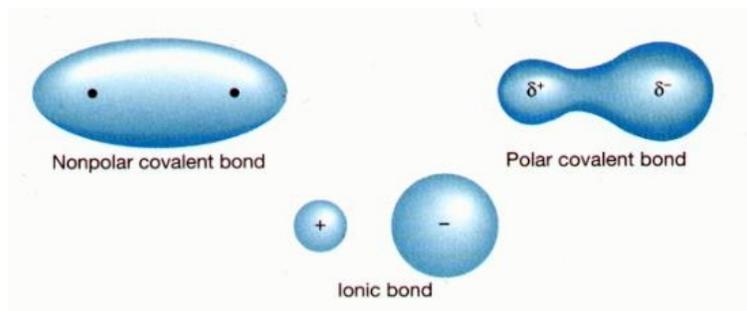
The bond polarity has an effect on the chemical properties of compounds.

23) Sec 9-7-3 - Predicting the Polarity of Bonds

When atoms are shared between atoms of the same element then they are shared equally. If electrons are shared equally, the bond is known as a **nonpolar covalent bond** or a **nonpolar bond**. The greater the difference in the electronegativities between two elements, the more polar is the bond between them. When the electronegativity difference is large (>1.7) then one atom is thought to have gained complete control of the electron and the bond is said to be ionic. (Sometimes the distinctions are fuzzy. The final description depends upon what we know about the compound or the bond.)

<u>Electronegativity Difference</u>	<u>Bond Polarity</u>
0.0 - 0.4	nonpolar covalent bond
0.4 - 1.7	polar covalent bond
>1.7	ionic bond

We can represent these differences in terms of electron clouds containing the electrons of the bond (similar to orbitals). The images below illustrate the progression of change from the nonpolar covalent bond through the polar covalent bond to the ionic bond.



Examples:

a) Ba - Br	$2.8 - 0.9 = 1.9$	ionic
b) C - N	$3.0 - 2.5 = 0.5$	polar
c) B - H	$2.1 - 2.0 = 0.1$	nonpolar
d) Be - Cl	$3.0 - 1.5 = 1.5$	polar*

{* - Although Be is a metal and one would expect that a compound like BeCl_2 to be ionic because it consists of a metal and nonmetal, generally it exhibits more of a molecular nature than an ionic one. This is an example of not sticking absolutely to the description of the electronegativity differences.}

A bond that is polar is often referred to as a **dipole** (literally two poles).

Section 9-8: Geometry of Simple Molecules

Why, after over one hundred years, do we still use Lewis structures to describe molecules? Not because chemists want to drive students insane and mystify the rest of

the world, but because we can use these representations of the arrangement of valence electrons in a molecule to help understand the **molecular structure** or **geometric structure** of a molecule, the **molecular geometry**. All of these terms refer to the three-dimensional arrangement of the atoms in a molecule. (This is much like our discussion of orbitals and the “volume” of space that electrons in atoms might occupy.

24) Sec 9-8.1 - Molecular Structure: The VSEPR Model

The structures of molecules play a very important role in determining their properties. Taste and smell are two properties that depend greatly on the shape of molecules. Biological activity often also depends upon structure with only a minor structural change determining the difference, say, between a molecule that is helpful to the body and one that might be poisonous.

It is often helpful to predict the structure of a molecule. One tool that chemists use is the **VSEPR** model or theory. The **Valence Shell Electron Pair Repulsion** model/theory is useful for predicting the structures of molecules. The main point of this model is that the structure is determined by minimizing the repulsions between the electron pairs in the molecule.

Some key points to remember:

- Molecular structure is the geometrical arrangement of the atoms of a molecule or ion in three dimensions. Molecular structure can be predicted using the fact that electron pairs associated with the valence shell of the central atom stay as far apart as possible.
- The bonded electrons and the lone pairs (unshared electron pairs) spread out around the central atom so that they are as far apart as possible. Electrons in double and triple bonds occupy only one position (that is, take up the same amount of space as a single-bonded electron pair). “A bond is a bond is a bond.”
- Unshared electrons pairs (“lone pairs”) of electrons are important. The unshared pairs strongly repel the bonded pairs, pushing them closer together. Each pair of unshared electrons causes the bonded electrons to be about 2° closer than expected.

The dot structures will help us to predict the structures by looking at the bonds and/or unshared pairs of electrons.

25) Sec 9-8.2 - Molecular Geometry

The **molecular geometry** of a molecule is the geometry described by the bonded atoms and does not include the unshared pairs of electrons. This is what we **SEE** when we actually look at the single molecule. However, this does not mean that the unshared pairs do not play an important role in the observed structure.

Possible Structures

Electron Pairs	Single Bond	Double Bond	Triple Bond	Lone Pairs	Shape
4	4	0	0	0	tetrahedral, 109.5°
4	3	0	0	1	pyramidal, 107°
4	2	0	0	2	bent or angular, 105°
4	0	2	0	0	linear, 180°
4	1	0	1	0	linear, 180°
4	2	1	0	0	trigonal planar, 120°
4	1	1	0	1	bent or angular, 105°

It is important to remember the **three basic shapes**, or the starting points, for these structures:

- tetrahedron** (4 things or the possibility of 4 things attached to the central atom)
- trigonal planar** (3 things or the possibility of 3 things attached to the central atom)
- linear** (2 things or the possibility of 2 things attached to the central atom)

Further, remember that anytime you have just two things connected (e.g.: H₂, O₂, N₂, CN⁻, CO, etc.) they will ALWAYS be linear no matter what kind of bond connects them.

There are additional shapes that we can talk about with additional numbers of electron pairs around the central atom. Phosphorus with 5 electron pairs and 5 things attached to the central atom starts with a trigonal bi-pyramid; and sulfur with 6 electron pairs and 6 things attached to the central atom gives an octahedron. These also show a progression of **final** shapes from these initial starting shapes, similar to what we see with 4 pairs of electrons. For our purposes you do not need to know these additional final shapes, just know that they also exist as part of VSEPR.

Examples - Give the molecular shape and the bond angle between bonded atoms for each of the examples used earlier.

- | | | |
|-----------------------------------|----------------------------------|----------------------------------|
| 1) PCl ₃ | 3) PO ₄ ⁻³ | 5) NO ₃ ⁻¹ |
| 2) ClO ₂ ⁻¹ | 4) SO ₂ | 6) H ₂ CNH |

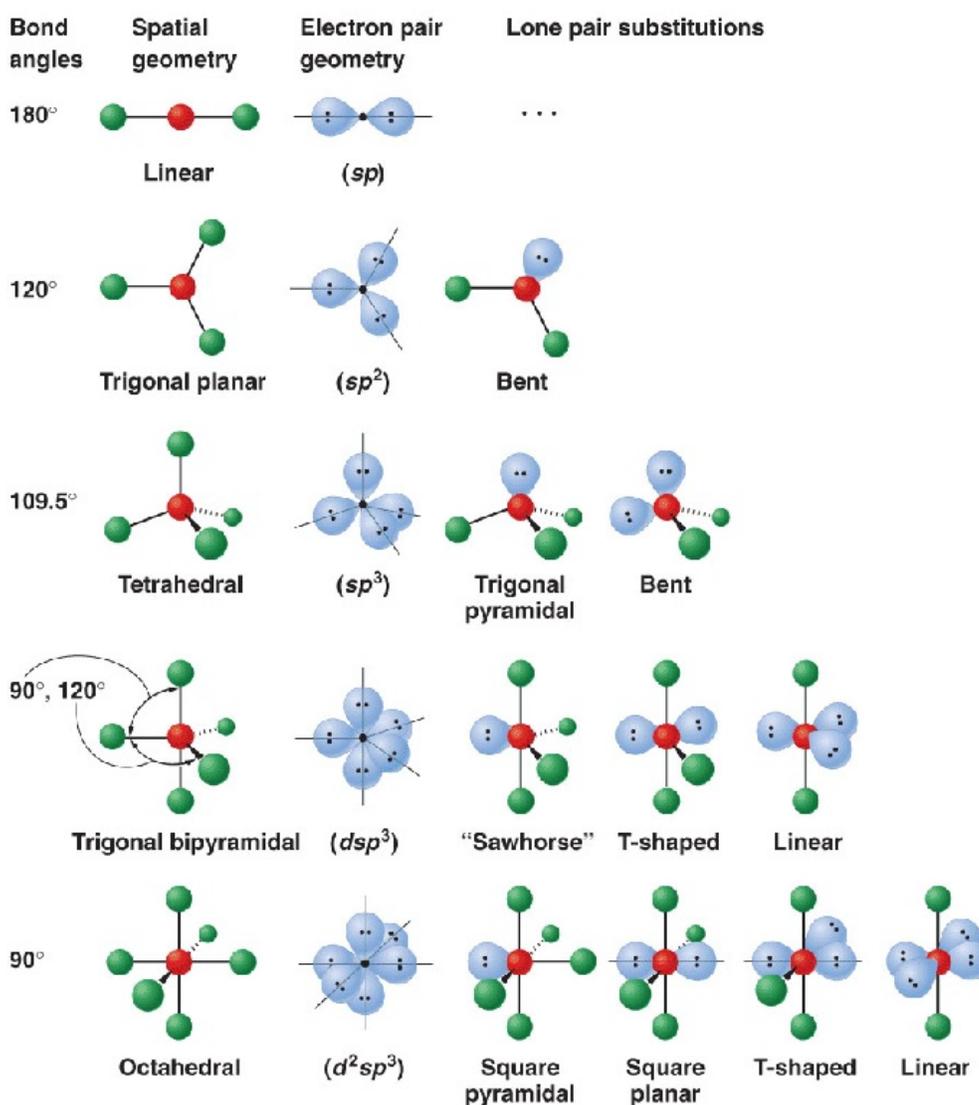
26) Other Basic Shapes

We have mentioned the fact that some elements do not seem to always follow the octet rule. The two we have specifically mentioned are P and S. These are said to have the possibility of 5 pairs of electrons and 6 pairs of electrons, respectively, around the atom. They specifically have basic shapes that are referred to as a **trigonal bipyramid** and an **octahedron**. Each of these “basic” shapes has a “family tree” similar to the instances we described in detail with 4 pairs of electrons.

27) Some Considerations

Sometimes the shapes match (remember that “a bond is a bond is a bond”) whether the start is 4 or 5 or 6 possible pairs of electrons around the center atom, and the final shapes appear the same after we look at the bonding and unshared pairs.

The simplest approach is always to look at the basic starting shape (most often the three options with 4 pairs of electrons) and then ask what shape results if you remove one or two bonds from the geometry (and replaced by unshared pairs). The resulting molecular geometries readily become apparent.



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Section 9-9: Polarity of Molecules

A polar bond in a molecule can be considered a force with both direction and magnitude. The result of the polarities of the bonds in a molecule and the geometric structure determines the polarity of a molecule.

28) Sec 9-9.1 - Nonpolar Molecules

In a molecule, the combined effects of the bond dipoles (the net dipole) are known collectively as the **molecular dipole** or the **dipole moment**. If the geometry of the molecule is such that equal dipoles cancel, then there is no molecular dipole and the molecule is nonpolar. The molecule has to be symmetrical. CF_4 and CO_2 are examples of this.

A molecule is also nonpolar if it is made entirely of nonpolar bonds, regardless of the geometry. Since the carbon-hydrogen bond of a hydrocarbon is essentially nonpolar, then the compounds containing only carbon and hydrogen can be considered nonpolar as well.

29) Sec 9-9.2 - Polar Molecules

Polar molecules occur when the dipole forces do not cancel. There can be two reasons for this to occur:

- The molecule is symmetrical but the terminal (attached) atoms are not the same and so the electronegativities are different. Thus, HCN (linear) and CHCl_3 (tetrahedral) are geometrically symmetrical, but because of the unequal dipoles the molecules are polar.
- The geometry of the molecule is v-shaped or a trigonal pyramid. The geometry leads to forces that do not cancel.

