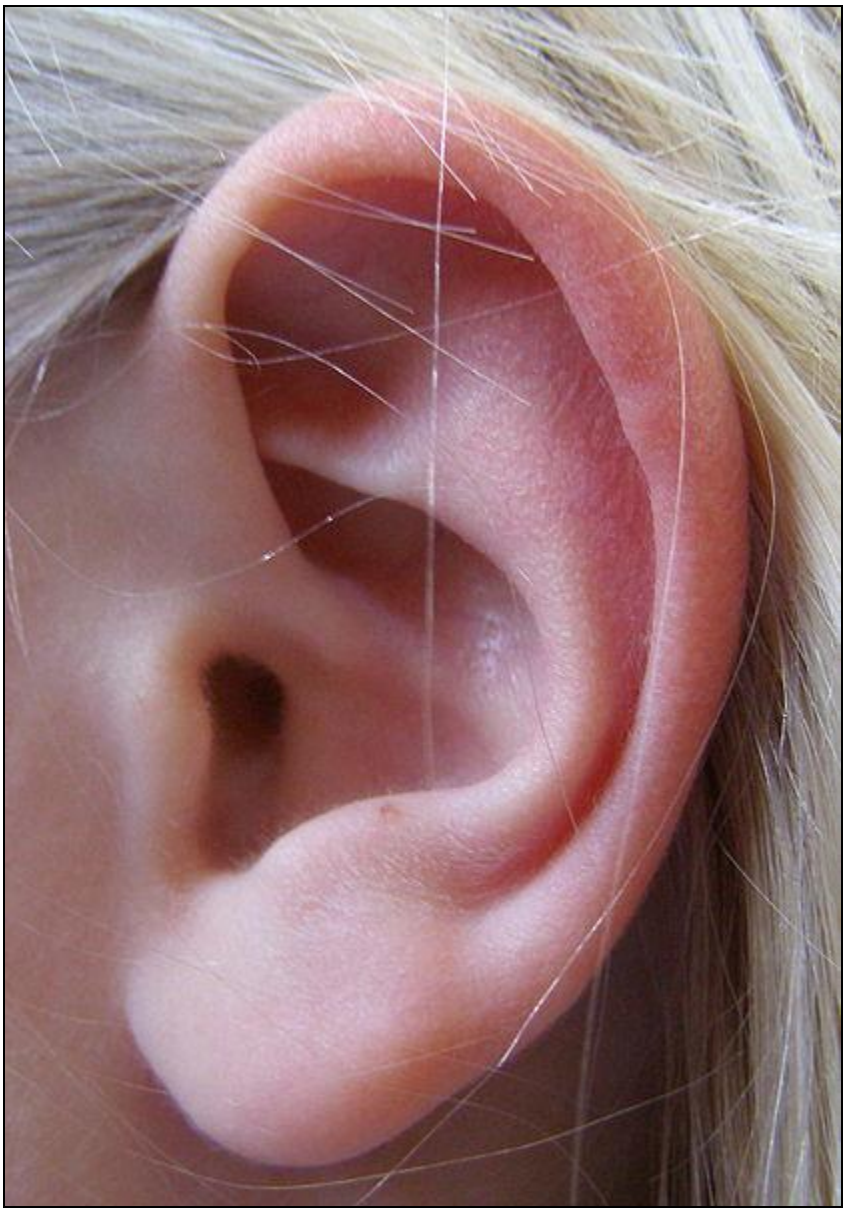
Chapter 9: Covalent Compounds



Ears contain lots of covalent bonds, because the main elements in their manufacture like to share valence electrons.

http://commons.wikimedia.org/wiki/File:Earcov.JPG

Chapter 9: Covalent Bonding

If you go back in time or space[1] you'll see the octet rule, which states that all elements want to gain or lose electrons to be like the nearest noble gas. Of course, if you could go back in time, you probably wouldn't care much about the octet rule, because you'd have a freakin' time machine. I'd go back to be the king of the Neandertals, but that's just me.

Anyway, let's see how the octet rule is related to covalent bonding.

Section 9.1: Covalent Bonding

Think back to the last chapter. Lithium is an element that wants to lose electrons while fluorine is an element that wants to gain electrons (because of, you guessed it, the octet rule). Lithium transfers its valence electron to fluorine, giving lithium a positive charge and fluorine a negative charge. These opposite charges are then attracted to one another, forming an ionic compound that lives happily ever after.

***Image 9.1**: Lithium and fluorine after the electron transfer has been completed. The other compounds are always telling them to "get a room."*

http://upload.wikimedia.org/wikipedia/commons/c/ca/Kiss_Briseis_Painter_Louvre_G278.jpg

Now, let's fast forward from the disgusting display that is LiF to the world of other elements. Let's talk about two fluorine atoms. Each fluorine atom has seven valence electrons and needs one more to be like the nearest noble gas. Neither fluorine is going to give the other fluorine an electron, so an ionic compound clearly won't be formed.

But what will happen? Will our fluorine atoms be stuck without being like noble gases? Will they forever feel the sting of being just a hair's breadth from what they want?

Nope. They'll form a covalent molecule. Let's investigate how this happens, in cartoon form:

[1] To the periodic table chapter

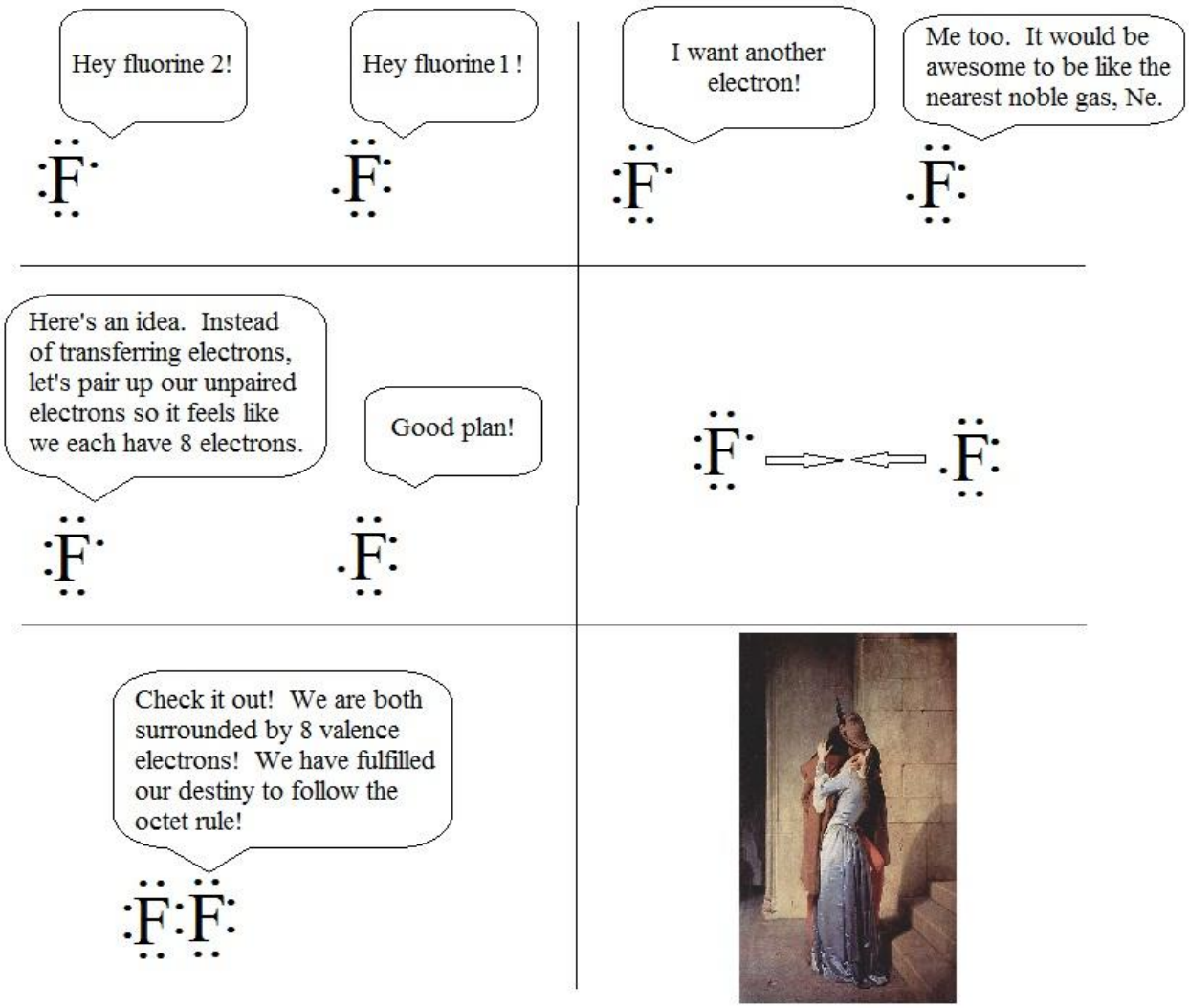


Figure 9.2: *Two fluorine atoms form an F_2 molecule via a single covalent bond.*

(http://commons.wikimedia.org/wiki/File:Francesco_Hayez_008.jpg)

Sounding like an Official Chemical Person:

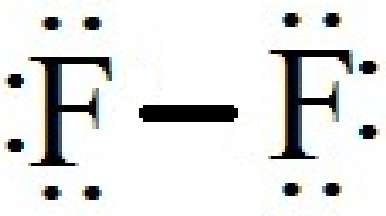
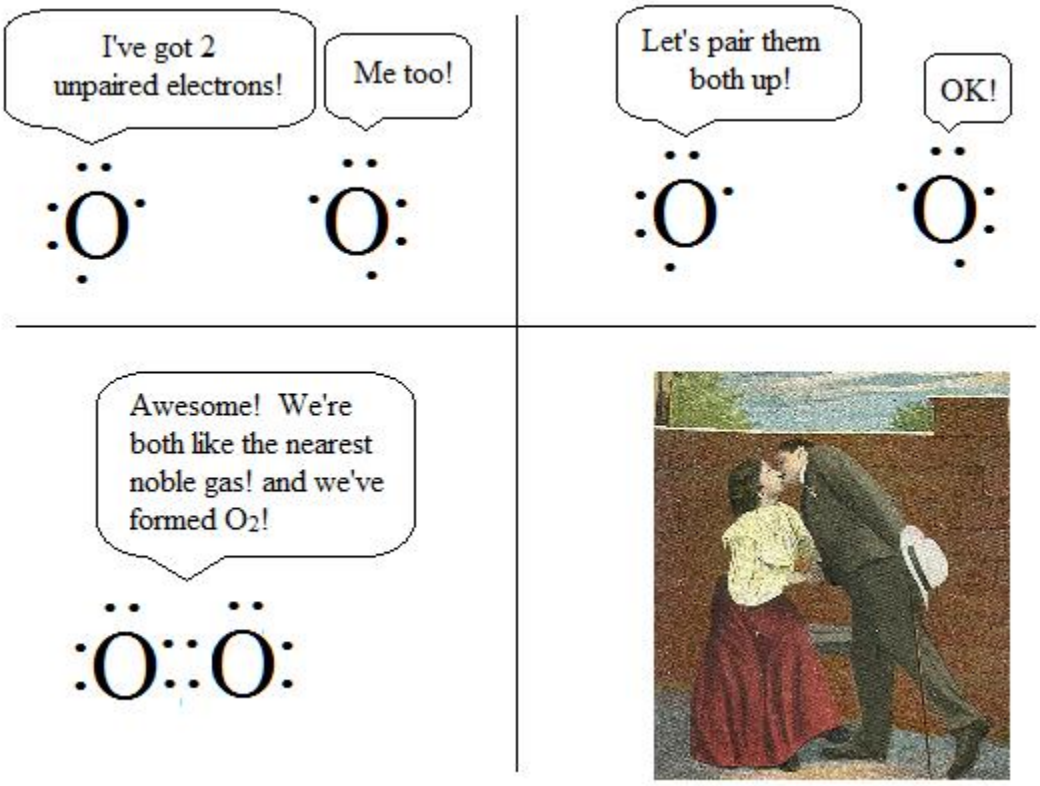


Figure 9.3: *Shared electrons in an ionic compound are usually shown as lines*

Though I showed a covalent bond as two electron dots between the fluorine atoms above, the usual convention is to draw covalent bonds as lines. Single bonds are shown as one line, double bonds as two lines, and triple bonds as three lines.

We can form molecules with double bonds using the same principle (Figure 9.3):



Triple bonds are also formed when two atoms have three unshared electrons, but I didn't feel like making another cartoon so you'll have to just imagine it.

A Couple of Good Things to Know:

Why does fluorine form ionic compounds with lithium while it forms covalent compounds with other nonmetals? The answer: Electronegativity.

Recall from the periodic table chapter where I mentioned that electronegativity is a measure of how much an atom grabs electrons from other atoms it has bonded with. Well, if two elements have very different electronegativities, this means that one wants to lose electrons and the other wants to gain electrons. In this case, an ionic compound is formed by the transfer of electrons.

However if you have two elements with similar electronegativities, both will want to pull electrons from the other. As a result, if they want to fulfill their octet rule destinies, they'll have to share electrons rather than transfer them. That's how covalent compounds are formed.

Also, always remember that while ionic compounds form crystal lattices, covalent compounds form molecules. This very much explains the vast difference in properties between each.

Section 9.2: Naming Covalent Compounds

Unlike ionic compounds, which are a total pain in the butt to name, covalent compounds are pretty easy. Let's take a look at how easy these things are.

Naming Binary Covalent Compounds:

A binary compound is one that contains only two elements. If you've got more than two elements, then it's not binary, and this section doesn't apply to you.

Basically to name these compounds, all you have to do is name the first element, name the second element with "-ide" at the end, and then tell people how many of each atom you have.[2]

For example, let's consider the case of P_2O_3. The name of this compound is "diphosphorous trioxide", or literally "two phosphorus atoms and three oxygen atoms." No polyatomic ions or Roman numerals to worry about!

For those of you who aren't familiar with the prefixes that you're supposed to know for this, here's a big chart o' awesomeness:

Number of atoms	Prefix you need
1	"mono-" (but only for oxygen if it's the second atom)
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

How do we know what naming system to use?

- If the compound starts either with a metal ion or NH_4, name it like an ionic compound.
- If the compound contains only nonmetals and doesn't start with H, name it like a covalent compound.
- If the compound starts with H, name it like an acid.

[2] Some notable exceptions: Water is H_2O, ammonia is NH_3, and methane is CH_4. There are lots of others, but these are the ones you need to know right off the bat.

Naming Acids

Acids are compounds that give off H^+ ions in water. Though there are fancy exceptions to this rule, the formulas of acids usually start with "H"[3], which makes them easy to identify. To name acids, do the following:

- If it doesn't contain oxygen, the name of the acid is "hydro[something]ic acid." For example, HF is "hydrofluoric acid", HCN is "hydrocyanic acid", H_2Se is "hydroselenic acid" and so forth.

Figure 9.4: *A bottle of hydrochloric acid on vacation in Brazil. According to Wikipedia, "a lot" of hydrochloric acid is used for "industrial stuff" every year.*

http://commons.wikimedia.org/wiki/File:Acido_cloridrico.jpg

- If the acid contains oxygen, it's named "[something][suffix] acid." Because polyatomic ions are what give these acids their oxygen, we need to know the names of these ions. If the name of the ion ends with "-ate", the suffix is "-ic" and if the name of the ion ends with "-ite", the suffix is "-ous." Thus, H_2SO_3, which contains the sulfite ion, is called "sulfurous acid." H_3PO_4, which contains the phosphate ion, is named "phosphoric acid."

Those Wacky Elements!

Figure 9.5: *Some of the elements have unusual formulas. The halogens and hydrogen are all diatomic, so they have the formula X_2 (for example, chlorine is Cl_2 and bromine is Br_2). Additionally, phosphorus has the formula P_4 and sulfur is S_8.*

http://commons.wikimedia.org/wiki/File:Sulfur-es67a.jpg

[3] You may have noticed that H_2O starts with an H. As we'll see later in the book, water can behave as an acid… or a base. In any case, we always call it water, never oxilic acid or something crazy like that.

Section 9.3: Lewis Structures

Because covalent compounds do a lot of cool chemistry, and this chemistry is largely dependent on the structures of these compounds, it's important that we know how to find these structures. Though there are a ton of different types of structures that you can draw for a compound, the one we will find most useful is the Lewis structure.[4]

Great Men Named Lewis

Figure 9.6: *Lewis Hamilton (1985-current) was the 2008 Formula One World Champion. Though he's a great driver on the track, his license was suspended for a month after he was caught driving 122 miles an hour.*

http://commons.wikimedia.org/wiki/File:Hamilton_2011_British_GP.jpg

Anyhow, here's how to draw a Lewis structure. We'll use NH_3 as our example.

- **Determine the number of valence electrons that are present in the compound.** In NH_3, we have a total of eight valence electrons – five for nitrogen and one for each of the three hydrogen atoms.[5]
- **Determine the number of "octet electrons" in the molecule** – in our case, it's 14 octet electrons. How do we know this? Use the following information:
    - Hydrogen has two octet electrons.
    - Beryllium has four octet electrons.
    - Boron has six octet electrons (or, if it's in a polyatomic ion, eight octet electrons).
    - All other elements have eight octet electrons.
- **Determine the number of bonding electrons in the compound.** This is done by subtracting the number of valence electrons from the number of octet electrons. In our example, this is 14-8 = 6 bonding electrons.

[4] Organic chemists and biochemists have a lot of different ways to draw structural formulas; the particular type of structure depends on the thing they're studying at the time.

[5] In case you've forgotten how to find valence electrons, it's the number of s- and p-electrons since the last noble gas. For example, calcium has two valence electrons, boron has three, and oxygen has six.

- **Determine the number of bonds in the compound.** This is done by dividing the number above by two. In our example, 6/2 = 3 bonds.
- **Draw the compound.** Because we love having rules for how to do stuff like this, use the following guidelines:[6]
    a. Hydrogen and the halogens always bond once.
    b. Oxygen's family and beryllium bond twice (unless it's a polyatomic ion, in which case they may bond once or twice).
    c. Nitrogen's family and boron bond three times (unless it's a polyatomic ion, in which case they may bond three or four times.
    d. Carbon's family bonds four times.

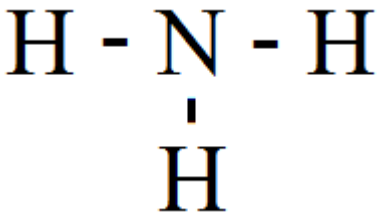


Figure 9.7: *As you can see, the three bonds that we said we needed earlier are shown in this structure. Even better, we followed the rules above, with nitrogen having three bonds and each hydrogen bonded once.*

- **Add dots to represent "lone pair" or "unbonded pair" electrons.** These are electrons which aren't involved in bonding, but are present on an atom so that it might have a full octet of valence electrons. Basically, this is done by just adding pairs of dots representing electrons until each element has the number of octet electrons we determined they needed earlier. In our example, we find that hydrogen needs no electrons (it wants only two octet electrons and there are two in each bond) and nitrogen needs a pair of electrons because it only has six octet electrons and wants eight). You can see this in the diagram below:

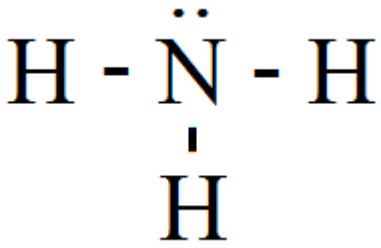


Figure 9.8: *Nitrogen wants a lone pair of electrons so it has a total of eight octet electrons (two from each bond for a total of six and two from the lone pair). The hydrogen atoms don't need lone pairs because they have their desired two electrons.*

- **For polyatomic ions, you need to figure out where the charged atoms are.** To do this, determine how many electrons each of them has around it (two per lone pair, one for each bond)

[6] There are exceptions to these rules, but they're pretty uncommon. We'll just pretend they don't exist, if that's OK with you.

and compare that to the number of valence electrons each wants. If the number of electrons around the atom is greater than the number of valence electrons, the atom is negatively charged. If it's less, then it's positively charged. You can check this out in the example of the hydroxide ion, OH^-:

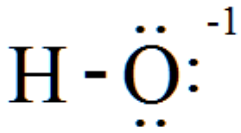


Figure 9.9: *The hydroxide ion. The oxygen atom has the negative charge, because it has 7 valence electrons surrounding it (three lone pairs and one bond) whereas neutral oxygen has six.*

Resonance Structures

Sometimes it's difficult to figure out where to put all of the bonds in a Lewis structure. In some cases this is because you just don't know what you're doing, but in other cases you may look at a structure and say to yourself "hey, this bond could go in several different places." If this bond is a double bond, you may be looking at the dreaded resonance structure.

Basically, resonance structures are a set of different Lewis structures, each of which show one of the ways that the molecule can be arranged. When you combine all of these resonance structures, you get a real idea of how the electrons in a molecule are actually arranged. Let's check this out by using the example of the nitrite ion, NO_2^{-1}. Because it's no fun to go through the math ugly step-by-step like we did above, I'll use the magic of embedded figures in the text to do that for me.

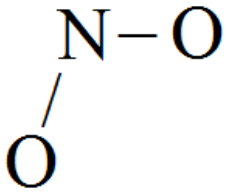


Figure 9.10: *Your math should show that you need to have three bonds. The problem: You can put the double bond between the nitrogen and either oxygen. What does this mean? Both answers are right, and you've got a bad case of resonance structures.*

To avoid the problem of having to pick one N-O bond over the other, draw two Lewis structures: One will correspond to the double bond being between one N-O bond and the other will correspond to the double bond being between the other N-O bond. These are your resonance structures for the nitrite ion:[7]

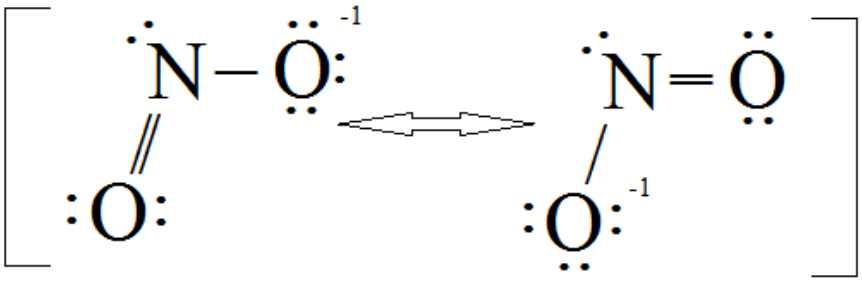


Figure 9.11: *The two resonance structures for the nitrite ion. Ain't they cute?*

[7] As mentioned above, the actual structure of the nitrite ion is somewhere between the two, with 1 ½ bonds between the nitrogen and –½ charge on each oxygen atom. Don't worry about this too much – it probably won't come up.

Expanded Octets:

Every so often, we run into a chemical compound with a Lewis structure that can't be solved using the method above. That's most likely because the central atom has an "expanded octet", meaning that it has more than eight valence electrons on it. This is caused because d-orbitals get involved in the bonding fun, making following the octet rule a more annoying experience.

Here's how you handle this sort of thing. Let's use the example of XeF_2:

- **Determine the number of valence electrons in the compound.** In this case, xenon has 8 and fluorine has 7 each (14 for both). The total valence electrons in the compound is 22.
- **Draw the molecule so that the central atom (usually the first thing in the formula) is bonded once to each of the other atoms.** In this case, Xenon will be bonded once to each of the fluorine atoms:

Figure 9.12: *What XeF_2 looks like denuded of valence electrons.*

- **Surround each of the outer atoms with pairs of electrons until they each have eight electrons.**

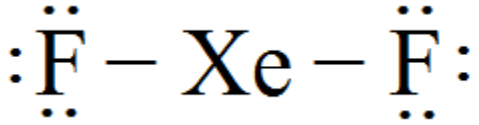


Figure 9.13: *XeF_2 after fluorine puts on pants, so to speak.*

- **Add the remaining electrons to the central atom in pairs until you run out.** Remember, the remaining electrons will be equal to the total valence electrons minus two electrons for each bond and lone pair:

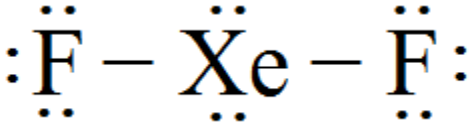


Figure 9.14: *The magical wonder that is xenon difluoride.*

Section 9.4: VSEPR Theory[8]

Believe it or not, chemists often find it useful to determine the shape of a molecule. This may seem like a waste of time, but it turns out that if we know the structure of a compound, we can usually figure out its properties and how it reacts when it meets other molecules.

[8] Pronounced "vesper".

The theoretical underpinning for determining the shape of a molecule is something known as VSEPR theory, where VSEPR stands for "Valence Shell Electron Pair Repulsion." Though this sounds like one of those terms that chemists used to make themselves look smarter, it's actually kind of a useful term.

Figure 9.15: *Benedictine monks celebrating vespers in Morristown, NJ.*

The part that says "valence shell electron pair" refers to the fact that we're dealing with the outer electron pairs on an atom – in other words, the lone pairs and bonds that are stuck to the atom. The "repulsion" part refers to the fact that electrons repel one another. When you put it all together, VSEPR theory tells us that the shapes of molecules are determined by how the outer electrons repel one another and try to move away from each other as much as possible.

For example, let's consider the example of CO_2. Depending on how we feel like drawing this molecule, we might come up with one of the following structures:

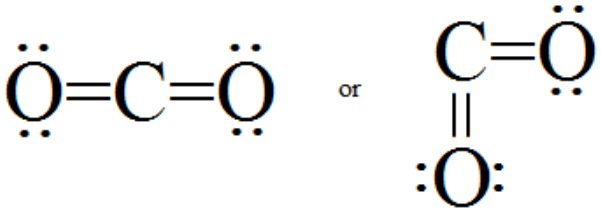


Figure 9.16: *Two technically-correct Lewis structures of carbon dioxide*

VSEPR tells us that only one of these drawings is correct. In the one of the left, we can see that the electrons in each C=O bond have retreated as far away from each other as possible, while in the drawing on the right we can see that the C=O bonds are at a 90 degree angle from one another. Because the electrons in each bond repel each other, the drawing on the left represents the actual structure of CO_2.

Let's go to another example of this to see what's going on. Using one of the resonance structures of the nitrite ion, we can see that VSEPR is followed:

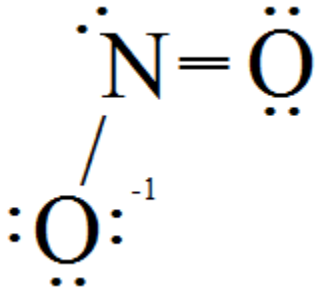


Figure 9.17: *The structure of the nitrite ion reflects the fact that the three sets of electrons on the nitrogen atom (one lone pair, one single bond, and one double bond) repel one another. This is why they're shown as being 120^0 angles apart from one another.*

So, how do we find the shape and bond angle for various chemical compounds? I'm glad you asked! Use the flowchart below to figure out what the bond angle and shape of your molecule of choice is:

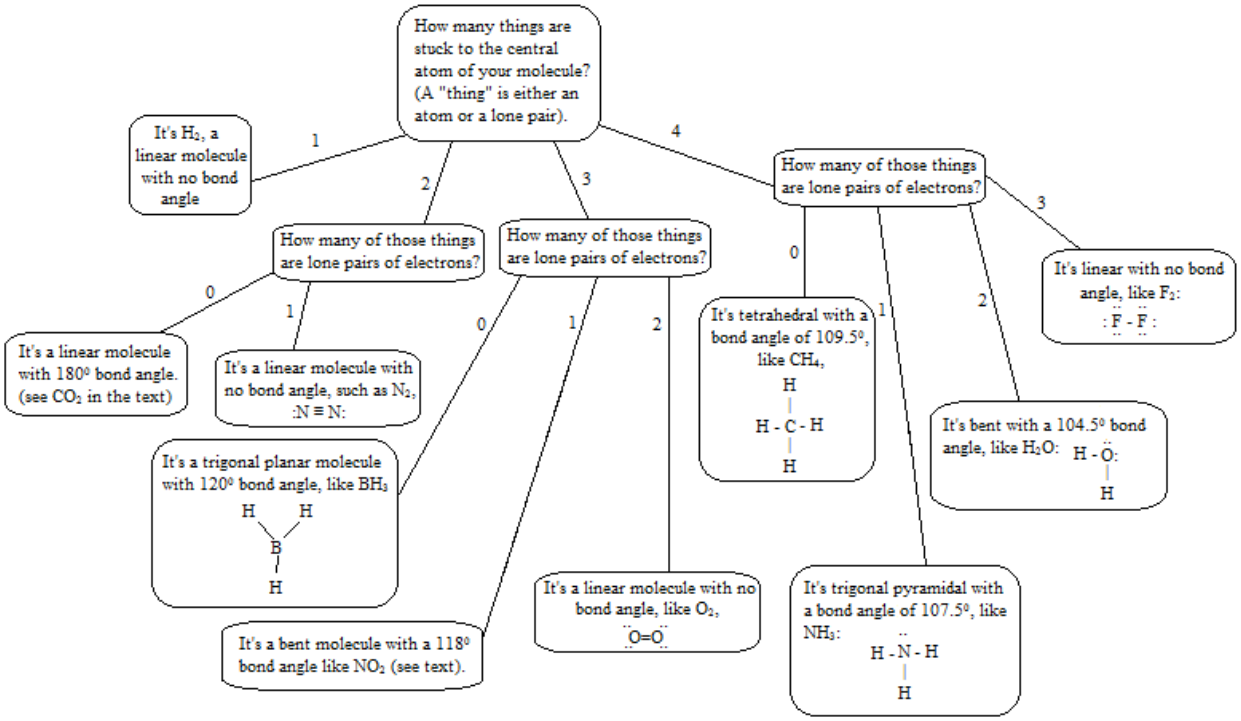


Figure 9.18: *A great big flow chart that tells you how to find bond angles and molecular shapes, VSEPR style. Note that molecules with expanded octets aren't included in this chart, because they're really not something you need to worry about much for a first-year chemistry class.*

> ***Spotlight On Something You'll Never Need to Know In Real Life***
>
> *Bonding in covalent molecules takes place in something called "hybrid orbitals", which are just regular s- and p-orbitals that have mixed together to form orbitals with properties somewhere in the middle. Using Figure 9.18, anything with four things on the central atom is sp^3 hybridized, anything with three things on the central atom are sp^2-hybridized, anything with two things on it is sp-hybridized, and hydrogen just uses unhybridized s-orbitals.*

You'll notice that when you compare the bond angles of CH_4 with the bond angle of NH_3, the angle changes to be two degrees smaller in NH_3. The reason for this is that the lone pair of electrons is a little more out and about, shoving the other atoms closer together than normal. This is why H_2O also has a bond angle that's three degrees smaller than NH_3- it's got another lone pair to jam those H-O bonds together a little harder.

Section 9.5: Polarity

Recall, if you will, the magical time when we discussed electronegativity.[9] Assuming your memory is good, you'll recall that electronegativity is a measure of how much an atom tries to grab electrons from other atoms it is bonded with. According to the octet rule[10], elements on the left side of the periodic table (metals) have low electronegativities while those on the right (nonmetals) have high electronegativities. Because nonmetals and metals have very dissimilar electronegativities, there is a transfer of electrons to form an ionic compound. Because two nonmetals will have similar electronegativities, there's a sharing of electrons to form a covalent compound.[11]

But what happens when two nonmetals have similar, but not identical electronegativities. The more electronegative atom will pull harder on the electrons than the less electronegative atom, causing an imbalance in the distribution of electrons. This, in turn, leads to a partial negative charge on the more electronegative atom because it has more than its share of electrons, and a partial negative charge on the less electronegative atom because some of its share of electrons has been pulled away from it. This situation is shown below in the case of an S-F bond.

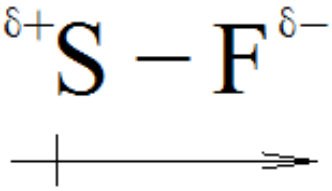


Figure 9.19: *I'm about to explain the stuff on this figure in the text. Just take a moment to enjoy my amazing Microsoft Paint skills.*

In figure 9.19, there are a couple of things you should be aware of:

- That funny arrow thing indicates the presence of a dipole. A dipole is what we call it when there's more negative charge in one place than another. In this case, the arrow points toward fluorine because fluorine is pulling the electrons in the S-F bond toward it using the power of its electronegativity.

- That δ^+ and δ^- stuff indicates the partial positive charge on the sulfur atom and the partial negative charge on the fluorine atom.

Whenever we have a covalent bond between two atoms with dissimilar polarities, it's referred to as a **polar covalent bond**.

> ***Did You Know?***
>
> *If there's an electronegativity difference between the two atoms in a bond, the bond will have some degree of polarity. If this difference is greater than about 1.8 Pauling units, we usually think of it as being an electrostatic attraction rather than a bond (i.e. ionic rather than covalent).*

[9] Specifically, during the magical chapter about the periodic table.
[10] Which says that all elements want to gain or lose electrons to be like the nearest noble gas.
[11] For those of you with bad memories, I talk about this very thing toward the beginning of this chapter, after the cartoons.

Molecular Polarity

So, we've talked about bonds being polar. Given that electrons can be unevenly distributed in a bond, can they also be unevenly distributed in a molecule?

Of course they can! Do you really think I'd write a section about this topic if it was impossible? Get a clue, buster.

Anyhow, a **polar covalent molecule** is any molecule where the electrons are unevenly distributed. This occurs in any asymmetric molecule. How can you tell if something is symmetric? Just draw the Lewis structure and look at the central atom – if any of the "things" stuck to it are different than each other, the molecule is polar.

Great Men Named Lewis

Figure 9.20: *Lewis the cat is the first cat known to have been put under house arrest, after previously having had a restraining order put on him by animal control officers in Connecticut. This picture is an artist's conception of what it would look like if Lewis the cat fought a monkey.*

http://commons.wikimedia.org/wiki/File:The_Monkey_and_the_Cat_by_Abraham_Hondius.jpg

Let's take a look at one famously polar molecule: water. If we draw the structure of water, we can see that it looks like this:

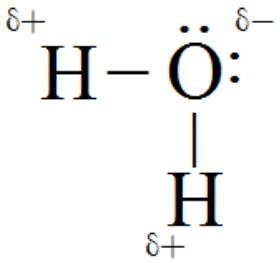


Figure 9.21: *Water, the wettest of the polar molecules.*

As you can see, oxygen has four things stuck to it: Two lone pairs of electrons and two hydrogen atoms. Because a lone pair of electrons is different from a hydrogen atom, this is a polar molecule. Likewise, if we look at carbon dioxide (Figure 9.22):

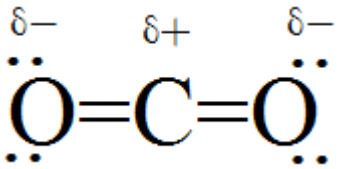


Figure 9.22: *Carbon dioxide.*

We see that it's totally symmetric around carbon (i.e. the two "things" that are stuck to it are both oxygen atoms), so it's a nonpolar molecule.

> ***Chemistry Fun(ish) Fact***
>
> *A covalent molecule can be nonpolar even while having polar covalent bonds. Use the example of carbon dioxide above – though the C=O bond is polar (oxygen is more electronegative than carbon), the symmetry of the molecule makes it nonpolar overall.*
>
> *A good rule of thumb (though not one that you see very often) is this: Molecules with lots of lone pairs on the central atom are generally more polar than those with fewer lone pairs. For example, water (which has two lone pairs on the oxygen) is more polar than ammonia (which has only one lone pair on the nitrogen atom).*

Section 9.6: The Properties of Covalent Compounds

Just as the properties of ionic compounds are determined by the fact that cations and anions are all jammed together in one big stable block, the properties of covalent compounds are determined by the fact that these compounds exist as molecules that more or less ignore one another.[12]

To imagine this in more concrete terms, let's think about ionic compounds as being like big locked chunks of Legu blocks[13] (Figure 9.23) In such an arrangement, the blocks are going to be hard to pull apart, which accounts for the hardness, brittleness, and high melting and boiling points of ionic compounds.

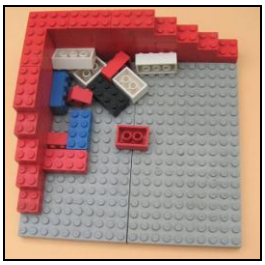


Figure 9.23: *Legu blocks, all stuck together. It looks like they're making a house, or maybe a castle. I wish I had some Legu blocks right now.*

http://upload.wikimedia.org/wikipedia/commons/2/2e/LEGO-02.jpg

[12] The forces that hold them together are called "intermolecular forces", but we won't worry about that right now.
[13] I use the term "Legu" because of a trademark dispute with another maker of toy blocks whom we won't name.

On the other hand, let's think about covalent compounds as being like a great big sack of sticky ping-pong balls.[14] In this case, we would expect the following properties:

- Covalent compounds have lower melting and boiling points than ionic compounds (often below room temperature). This is because it doesn't take much energy to pull these ping-pong ball molecules apart from one another.

- Covalent compounds tend to be less hard and brittle than ionic compounds. This is because those ping-pong ball-molecules can shift around when hit with an external force.[15]

- Covalent compounds are more likely to burn than ionic compounds. The reasoning is simple: Carbon and hydrogen have nearly identical electronegativities, so they form a vast number of covalent compounds with one another.[16] Since carbon and hydrogen are required for a compound to burn, we would expect for covalent compounds to be more likely to burn than ionic compounds (Figure 9.24).

Figure 9.24: *This flaming car contains covalent compounds in the seats, gas tank, and tire. In case you were worried, the driver got out, so he's not part of the flaming debris seen here.*

http://commons.wikimedia.org/wiki/File:Lightmatter_carbq.jpg

- Covalent compounds don't tend to conduct electricity. Electricity is conducted through the movement of charges (either ions or electrons), and in a covalent compound there are no ions present and electrons have no way to move around. This is why covalent compounds are almost uniformly insulators off electricity.[17]

[14] We're saying that they're sticky to account for the weak intermolecular forces that attract covalent molecules to one another, as mentioned in footnote 12.
[15] This isn't to say that covalent compounds are *objectively* soft or squishy. For example, if I were to hit you in the head with a big block of ice, you wouldn't think of it as particularly soft, even though it isn't quite as hard as you would expect from an ionic compound.
[16] These are called "organic compounds."
[17] Yes, even water, which is a covalent compound, isn't a good conductor of electricity. So why will you fry when you put the radio in the bathtub with you? It's because the water in the bathtub contains dissolved ionic compounds, which allow electricity to travel through water.