Chapter 7 – Chemical Bonding and Molecular Geometry

We now address one of the most important topics in this course: chemical bonding. That is: what causes two atoms to stick together? One of the simplest statements that describes chemistry is "Chemistry is the breaking of existing bonds and the making of new bonds." This is how reactant molecules are converted to product molecules. As I've said in class many times, systems tend to go to the lowest energy state possible and opposite charges attract. These statements will be very important in this chapter. Chapter 5, thermochemistry, discussed the heat changes associated with chemical processes. The heat was energy liberated when stronger ones replaced weaker bonds. We now will begin to explore the different types of chemical bonds (ionic and covalent) and what influences their strengths. A common misunderstanding is that one of these types of bonds is stronger, on average, than the other. That really isn't true. We'll also see that the two types of bonds are really two faces of the same coin. Finally, the simplest way to view a chemical bond is the attraction of the nucleus on species 1 for one or more electrons on atom 2, and vice-versa.

7.1   Ionic Bonding

We begin with a descriptive discussion of bonding. Ionic bonds are those between ions. Here the attraction is between oppositely charged particles and is treated as a purely electrostatic interaction. As you might expect, in most cases the higher the ion charge, the stronger the bond. Generally speaking, ionic compounds tend to be hard and brittle. They are poor electrical conductors as a solid, but good in solution and when molten. They have high melting and boiling points. Many dissolve in water, but the statement that "most readily dissolve in water" (p. 344) is probably not true. Go back to the solubility rules in Chapter 4.2, p. 182, and my notes) to see why. The simplest

way to picture this is as oppositely charged spheres touching one another. As the book notes, the ions in a salt arrange themselves into a rigid lattice (p. 345). We will see in Section 7.5 how this lattice affects bond strengths and the physical properties of salts. The electronic structure of ions is essentially a repeat of electron configurations from Chapter 6.

7.2 Covalent Bonding

Covalent bonds are those between neutral species. Here the electrons reside between the atoms and, as we shall see, the nuclei of the two atoms are pulled towards one another. The simple view of covalent bonding differs from ionic bonding in that the electrons lie between the nuclei. For a homonuclear diatomic molecule (e.g. H_2), the bond shape would be a 3-dimentional oval. The electron density would be greatest exactly half-way between the nuclei and drop off as you move toward the nuclei.

Pure vs. Polar Covalent Bonding

There exists a situation between ionic bonding (where one atom essentially strips an electron off the other atom) and pure (or nonpolar) covalent bonding (where the two atoms have exactly the same hold on their electrons). "Polar" covalent bonding is a situation where one atom (A) pulls on its electrons a little more than the other atom (B) pulls on its electrons. In this case, the electron density still resides between the two atoms, but now instead of being exactly in the center, the maximum electron density is shifted towards atom A. This unequal sharing of electron density is called a polar covalent bond.

Electronegativity

Electronegativity, χ, is the ability of a bound atom to draw electron density towards itself.

Electronegativity depends on both the ionization energy and the electron affinity of the atom. Atoms with large IEs and EAs tend to hold onto electrons well and have high electronegativities. Those with low IEs and EAs have low electronegativities. In fact, one method of calculating electronegativity simply takes the average of ionization energy and electron affinity of an atom (χ = ½(IE + EA)), then prorates all values to a scale where fluorine has a value of 4.0.

Fluorine has an electronegativity defined as 4.0 (no units), the highest possible value, while cesium has the lowest value, 0.7. All other elements have values calculated relative to fluorine. Electronegativity increases up and right across the periodic table. Electronegativities of transition metals are largely meaningless and you may ignore them.

For two bound elements, a very small $\Delta\chi$ (say ≤ 0.2) means the bond is (essentially) nonpolar. Bond polarity generally increases with $\Delta\chi$. The following pictures illustrate two ways of depicting the shift in electron density. In the first, the symbol δ means "partial." In the second, the shape indicates electron density shifted towards fluorine.

$$\overset{\delta^+ \quad \delta^-}{\text{H-F}} \qquad \overset{+}{\text{H}} \longrightarrow \text{F}$$

There has always been a temptation to set a dividing line between polar covalent and ionic bonding. The problem is that there are exceptions no matter where you draw the line. It is made more difficult because there are different ways to calculate electronegativity. The dividing line for $\Delta\chi$ is probably between 1.5 and 2.0, but it's best to look at the elemental composition as much as the $\Delta\chi$ value.

Optional: You don't need to memorize individual values, but here is a good rule of thumb for remembering electronegativity values. You must remember F = 4.0 and H = 2.1. Going down the

halogens subtract 0.5 for each element and going left across the period subtract 0.5. For Groups 5 & 6, subtract 0.4 going down, for Groups 3 & 4, subtract 0.3 going down the group, and for Groups 2 and 1 subtract 0.2 and 0.1, respectively. While this gives values different from your book, (i) electronegativity is a qualitative concept and (ii) it works fairly well in predicting relative bond polarities.

7.3   Lewis Symbols and Structures

It turns out there is a simple way to predict the numbers and types of covalent bonds in most molecules. We learned in Chapter 2, that we could use the group number to predict the charge on anions and cations. Something very similar works in molecules, which we will now address. Remember that valence electrons are those past the noble gas core and that these electrons are the ones that are chemically active. When drawing bonded atoms, Lewis symbols can help determine the number of chemical bonds in a molecule. A Lewis symbol is composed of the atomic symbol of a main group element, a number of dots equal to the number of valence electrons on the atom, and an imaginary square around the atomic symbol.

$$\text{Li}\cdot \quad \cdot\text{Be}\cdot \quad \cdot\dot{\text{B}}\cdot \quad \cdot\dot{\text{C}}\cdot \quad \cdot\dot{\ddot{\text{N}}}\cdot \quad \cdot\ddot{\ddot{\text{O}}}\cdot \quad :\ddot{\ddot{\text{F}}}\cdot \quad :\ddot{\ddot{\text{Ne}}}:$$
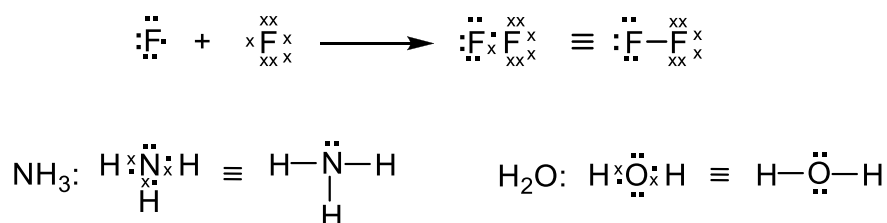
Every element in the same group will have the same sequence of electrons around it. Thus, every alkali metal will have as a Lewis symbol, the atomic symbol followed by a single dot.

It has long been known from experiments that when forming compounds, an atom tends to gain, lose, or share electrons such that its valence shell has the same number of electrons as the nearest noble gas. Excluding d-electrons, the valence shell will hold 8 electrons and this is called the <u>octet</u> <u>rule</u>*. The rule almost always works for 2nd row elements and usually does for lower rows. The total*

equals 8 because each valence shell contains 1 s and 3 p orbitals and filling them requires 8 electrons.

Hydrogen is the one exception to the octet rule among the main group elements. Possessing a single

s orbital, it requires only two electrons to attain a noble gas electron configuration.

Some examples of Lewis structures include:

$$:\ddot{\text{F}}\cdot \ + \ {}_{\times}^{\times\times}\underset{\times\times^{\times}}{\text{F}}{}^{\times} \ \longrightarrow \ :\ddot{\text{F}}{}_{\times}^{..}\underset{\times\times^{\times}}{\text{F}}{}^{\times} \ \equiv \ :\ddot{\text{F}}-\underset{\times\times^{\times}}{\text{F}}{}^{\times}$$

NH_3: $\text{H}\overset{..}{\underset{\times}{\text{N}}}{}_{\times}^{\times}\text{H} \equiv \text{H}-\overset{..}{\text{N}}-\text{H}$

H_2O: $\text{H}\overset{..}{\underset{..}{\text{O}}}{}_{\times}\text{H} \equiv \text{H}-\overset{..}{\underset{..}{\text{O}}}-\text{H}$

The sharing of one pair of electrons is called a single bond. The sharing of two pairs of electrons

is a double bond. The sharing of three pairs of electrons is a triple bond.

O_2: $\overset{..}{\underset{..}{\text{O}}}\overset{\times\times}{\underset{\times\times}{::}}\overset{\times\times}{\underset{\times\times}{\text{O}}}$ or $\overset{..}{\underset{..}{\text{O}}}=\overset{..}{\underset{..}{\text{O}}}$

N_2: ${}_{\times}^{\times}\text{N}{}_{\times}^{\times}\text{N}:$ or $:\text{N}\equiv\text{N}:$

Multiple bonds are always shorter and stronger than single bonds between the same two

elements. The added strength makes it more difficult to break these molecules apart than those with

only single bonds between the same two elements. Electrons not used in bonding are called

nonbonding electrons or lone pair electrons. These structures are called Lewis structures.

Drawing More Complex Lewis Structures

1. Add up the total number of valence electrons on all atoms. If you are working with a polyatomic

    ion (e.g. acetate or ammonium ions), add an electron for each negative charge or subtract an

    electron for each positive charge.

2. Write the atomic symbols of the atoms in the correct spatial arrangement.

3. Draw a line to connect each pair of bonded atoms. Subtract 2 electrons from the total for each

    bond drawn.

4. If the total from (3) equals that from (1) stop. If not, see if the octets can be completed by placing the remaining electrons on the atoms. If so, do it and stop.

5. If not, change one or more single bonds to multiple bonds and recalculate until all atoms (except H) have an octet. It is important to remember that hydrogen always forms exactly one bond.

NH_3: 5 + 3(1) = 8 electrons

$$H{-}N{-}H$$
$$|$$
$$H$$

$8e^- - 3(2e^-) = 2e^-$

$$H{-}\ddot{N}{-}H$$
$$|$$
$$H$$

The nitrogen now has an octet of electrons.

HCN: 1 + 4 + 5 = 10 electrons

$$H{-}C{-}N$$

$10e^- - 2(2e^-) = 6e^-$

$4e^- - 2e^- = 2e^-$

$$H{-}C{\equiv}N \longleftarrow H{-}C{=}N$$

$6e^- - 2e^- = 4e^-$

$$H{-}C{\equiv}N\colon$$

The carbon and nitrogen now each have an octet of electrons.
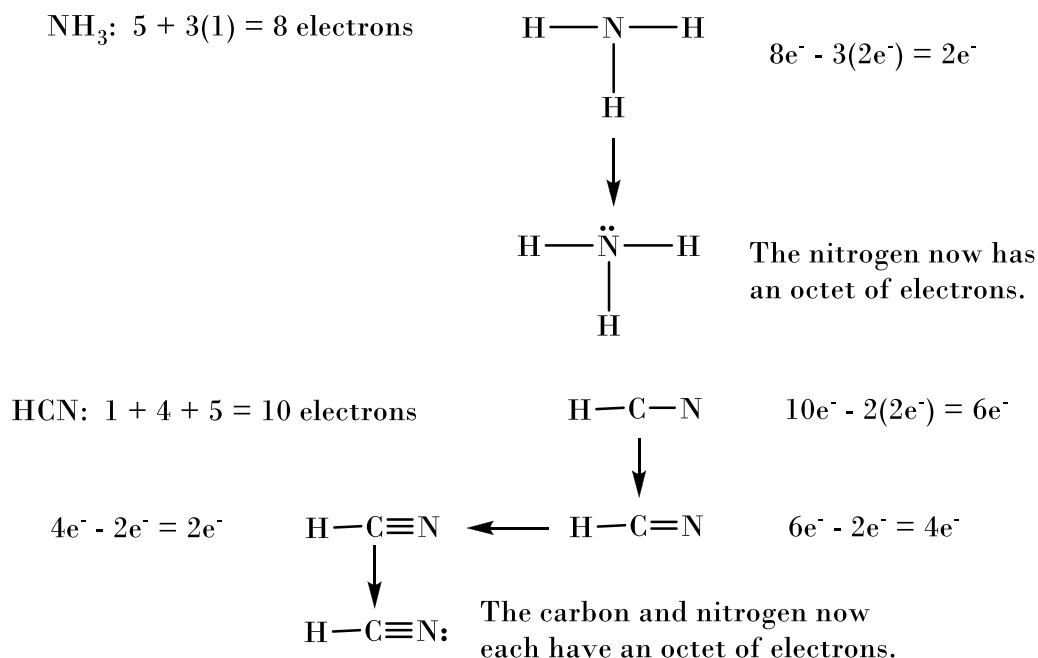
Being able to do this is critical to passing organic chemistry.

It is worth remembering that Group IVA elements tend to form 4 bonds, Group VA three bonds, Group VIA two bonds, and Group VIIA one bond (one bond for each unpaired electron). In the above molecules, Xs and dots were used to distinguish between electrons on different atoms. In reality, no such distinction exists. Nevertheless, using this system may be helpful initially and in determining formal charges.

Octet Rule Exceptions

Odd Electron Molecules

A relatively small number of compounds have an odd number of valence electrons. These compounds are sometimes called free radicals or, more simply, radicals. You may have heard of these

compounds from advertisements for vitamins or skin care products. In general, odd electron compounds display very high reactivity and can do great damage in biological systems, particularly to DNA. Normally when odd electron compounds form, two of the molecules will combine and the odd electrons will pair in a bond. (e.g. Fluorine atoms have 7 electrons. The unpaired electrons on two fluorine atoms pair to form a single bond.) The following type of molecule is rarely observed in General Chemistry, but will be a little more common in later years. Nitric oxide is a fairly typical odd electron compound.

$$\ddot{N} = \ddot{O} \quad \longleftrightarrow \quad \ddot{N} = \ddot{O}$$
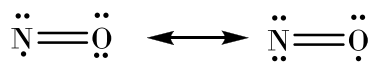
Which of these forms is favored and why?

Electron Deficient Compounds – skip these because there are nearly no examples

Hypervalent Molecules (Those with Atoms with More Than an Octet)

These are the most common of the exceptions and is sometimes called an "expanded octet." In most cases, a central atom possesses the extra electrons.
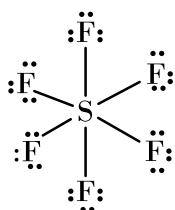
Sulfur has 12 valence electrons

Expanded octets occur most frequently when highly electronegative elements are bound to a central atom (e.g. F, O, Cl, etc.). They occur because of the energy derived from the additional bonds more than compensates for the energy required to promote the electron to a higher energy orbital. The book's description of the sulfate ion is incomplete. A fuller version is
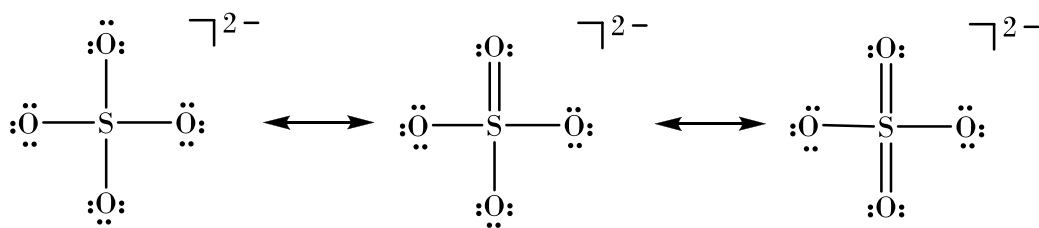
1 resonance form   4 resonance forms   6 resonance forms

$FC_S = 6 - 4 - 0 = +2$ $FC_S = 6 - 5 - 0 = +1$ $FC_S = 6 - 6 - 0 = 0$

$FC_O = 6 - 1 - 6 = -1$ $FC_O = 6 - 1 - 6 = -1$ $FC_O = 6 - 1 - 6 = -1$ single bond

$FC_O = 6 - 2 - 4 = 0$ $FC_O = 6 - 2 - 4 = 0$ double bond

This ion has a total of 11 resonance forms (see next section). The first resonance structure has the advantage of all atoms possessing an octet of electrons, but is raised in energy by all atoms possessing a formal charge, one of which is large. The final structures have the lowest formal charges (see next section) but are raised in energy by having a sulfur atom with 12 valence electrons. The sulfate ion would have an intermediate structure with all bond lengths equal and somewhat shorter than an S-O single bond.

7.4   _Formal Charges and Resonance_

Formal Charges

It is important to keep in mind that formal charges are _not_ real charges. They are a bookkeeping system for electrons. When two atoms bind together covalently, each atom usually contributes one electron to the bond. However, occasionally one of the atoms contributes both electrons. These bonds are called _coordinate covalent_ or _dative_ bonds. When this happens, electron density shifts away from the atom which contributes both electrons towards the atom that contributes none. The effect is a little like a small difference in electronegativity. Formal charge is calculated as follows:

i)   Determine the total number of valence electrons on all atoms.

ii)   Subtract from that the number of bonds to the atom <u>and</u> the number of electrons not involved in bonding on the atom.

Formal charge = (total valence e⁻) − (# bonds) − (e⁻ in lone pairs)

The sum of the formal charges on each atom in a molecule or ion will equal the overall charge on the atom or ion. Let's look at the ammonia example from earlier.

NH3: Each hydrogen has one valence electron, forms one bond and has no unbound electrons.

FC = 1 - 1 - 0 = 0

The nitrogen has 5 valence electrons, 3 bonds, and 2 unbound electrons.

FC = 5 - 3 - 2 = 0

Now consider the compound H_3N-BF_3. It is sometimes written $H_3N{\rightarrow}BF_3$ because the electrons for the bond between nitrogen and boron come only from nitrogen.

Each hydrogen has one valence electron, forms one bond and has no unbound electrons.

FC = 1 - 1 - 0 = 0

Each fluorine has seven valence electrons, forms one bond and has six unbound electrons.

FC = 7 - 1 - 6 = 0

The boron has 3 valence electrons, forms 4 bonds, and has no unbound electrons.

FC = 3 - 4 - 0 = -1

The nitrogen has 5 valence electrons, forms 4 bonds, and has no unbound electrons.

FC = 5 - 4 - 0 = +1

So what does this mean? It certainly <u>**does not mean**</u> that the boron atom is a lot like an anion and the nitrogen atom is a lot like a cation. It doesn't necessarily even mean that the boron has a

partial negative charge and the nitrogen a partial positive charge. What it does mean is that the boron atom has more electron density on it than you might have at first guessed based only on their positions on the periodic table (or electronegativities) and the nitrogen atom less electron density than a first guess.

There are a few rules for placing formal charges on atoms:

1) *The smaller the formal charges the better. Ideally, in a neutral molecule, each atom will have a zero formal charge.*

2) *When formal charges are placed, it is usually best to place the most negative formal charge on the most electronegative atom, and the most positive formal charge on the least electronegative atom.*

3) *Formal charges should be adjacent, when possible.*

<u>*Resonance*</u>

All of the bonds we've talked about so far have been localized bonds. <u>Localized bonds</u> occur when the bonding electrons distribute between only two atoms. Electrons that can move between more than two atoms yield <u>delocalized</u> bonding. This is important because sometimes it is possible to draw two different Lewis structures that are reasonable. For example, the common organic molecule benzene has 2 resonance forms (see below). While they might initially look identical (i.e. all you would have to do is rotate the molecule 60°), they aren't. Imagine if two adjacent carbon atoms were ^{13}C and the others were ^{12}C, now they are clearly different.
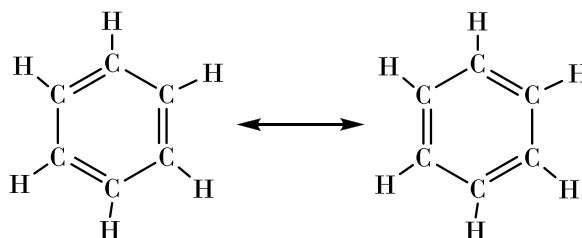
Energetically similar structures with the same atom connectivity are called <u>resonance</u> <u>structures</u>. The word "resonance" is an unfortunate one because it implies the molecules resonate between different forms. Again, they don't, there is only one structure. Resonance forms simply show the inadequacy of attempts to depict them. In general, resonance forms with smaller formal charges are favored over those with larger ones. Likewise, the closer formal charges are to each other on the molecule, the better. In each case, the goal is to minimize the separation of charge.

Again, there are three requirements for resonance structures: (i) the atom connectivity must be the same for each, (ii) the bonding must be reasonable, and (iii) they must be energetically similar. The nitrate ion has three resonance forms.
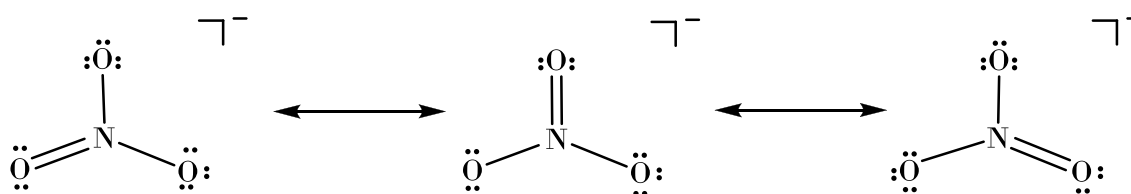
As you can see, it appears that the double bond rotates around the ion. Thus, all three criteria are met. The same atoms bind to each other (3 N-O bonds, no others). Each atom has a complete octet, so the bonding is likely to be acceptable. Since each structure possesses two N-O single bonds and one N-O double bond and the spatial arrangement of the atoms is identical in all three structures, the energy of each structure must be the same as the others. As we shall see shortly, not all resonance structures will be so similar.

7.5   <u>Strengths of Ionic and Covalent Bonds</u>

Something I said at the beginning of this chapter bears repeating. On average, ionic and covalent bonds are comparably strong. We'll discuss why in this section.

Covalent Bonds

The energy required to break a particular bond within a gas phase molecule is called its <u>bond energy</u>, D. It is sometimes called <u>bond enthalpy</u>. One would expect that the energy required to break an X-Y bond would depend the atoms bound to X and Y. While true to some extent, the attached groups usually have only a small effect on bond energy. Table 7.2 (p. 368-369) lists bond energies for numerous common bonds. The values represent an average for that bond in many different molecules. Bond energies tell us something about reactivity. As bond energies increase (stronger bonds) reactivity decreases. Thus, reactions frequently happen at the weakest bond in a molecule.

The correlation between bond energy and bond lengths is generally not very good, with one important exception. One would expect that as bond strength (energy) increases, the bond lengths would become shorter. For a multiple bond progression (single $\rightarrow$ double $\rightarrow$ triple), there is a strong correlation (see Table 7.3, p. 369). For small energy changes, the correlation is poor.

In Chapter 5, you learned about energy changes associated with chemical reactions and that nearly all reactions are exothermic (release heat). Where does that energy come from? In all reactions, existing bonds are broken and new bonds are formed. Almost invariably, the new bonds are stronger than the old ones and that energy difference accounts for most of the heat released. The difference in bond energies for reactants and products gives a quick and reasonably accurate estimate of the heat of reaction.

$$\Delta H_{rxn} \approx \Sigma D(bonds\ broken) - \Sigma D(bonds\ formed)$$

Note the order. It occurs this way because bond energies are always positive.
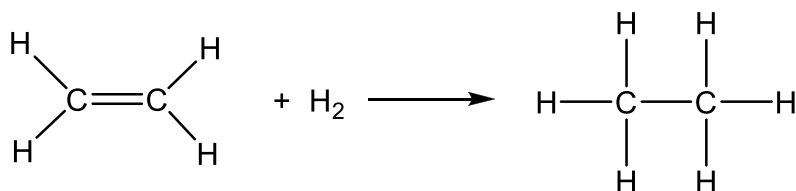
$$\Delta H_{rxn} \approx [D(C=C) + D(H\text{-}H)] - [D(C\text{-}C) + 2D(C\text{-}H)]$$

$$\approx [(1 \text{ mol})(611 \text{ kJ/mol}) + (1 \text{ mol})(436 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(345 \text{ kJ/mol}) + (2 \text{ mol})(415 \text{ kJ/mol})]$$

$$\approx -128 \text{ kJ} \quad (\textit{actual value is -137 kJ, less than 10\% higher than the estimate})$$

Thus, bond energies usually encompass the large majority of the energy change that occurs in chemical reactions.

Ionic Bond Strength and Lattice Energy

The energy of attraction for any two ions is given by:

$$E = k\frac{Q_1 Q_2}{d}$$

where Q1, Q2 are the charges on the ions and d is their distance of separation. This equation is consistent with what we would expect. Within a crystal lattice this equation becomes

$$\Delta H_{lattice} = \frac{CZ^+ Z^-}{R_0}$$

where C is a constant that takes into account the geometry of the lattice and part of the charge. Z^+ and Z^- are the integral ion charges, and R_0 is the internuclear distance between the interacting ions. Since the ions in a simple binary salt (e.g. NaCl) are oppositely charged, their energy of interaction must be negative and thus favorable. This holds true for all salts even when there is more than one ion of the same charge.

<u>*Lattice Energy*</u>

Ionic compounds typically have very large, negative heats of formation (Appendix G, p. 1211).

We will now examine the origin of this property. The following diagram, called a Born-Haber cycle,

provides the easiest way to explain the large energy release. It is an application of Hess' Law. The

example used here is cesium metal reacting with fluorine gas. This figure shows the same process as

displayed on p. 373, but using a different pictorial representation. Either method is fine to use.

$$Cs_{(g)}^+ \quad + \quad F_{(g)}^-$$

$$\uparrow DH_{IE}^\circ \qquad \uparrow DH_{EA}^\circ \qquad \qquad -DH_{LE}^\circ$$

$$Cs_{(g)} \quad + \quad F_{(g)}$$

$$\uparrow DH_{vap}^\circ \qquad \uparrow DH_{BE}^\circ$$

$$Cs_{(s)} \quad + \quad \tfrac{1}{2} F_{2\,(g)} \quad \xrightarrow{\;DH_f^\circ\;} \quad CsF_{(s)}$$
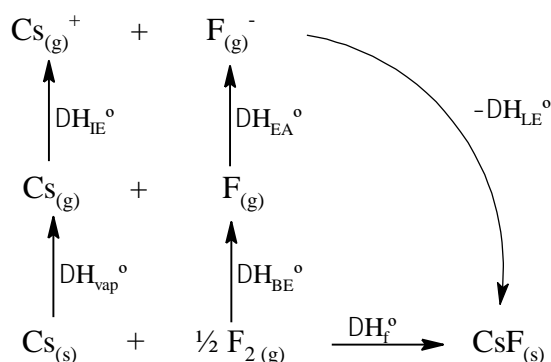
ΔH_{LE}° = *lattice energy (defined below)* $\qquad \Delta H_{IE}^\circ$ = *ionization energy*

ΔH_f° = *heat of formation* $\qquad\qquad\qquad \Delta H_{EA}^\circ$ = *electron affinity*

ΔH_{vap}° = *heat of vaporization of the metal* $\qquad \Delta H_{BE}^\circ$ = *bond energy for the halogen*

Thus, from Hess' Law: $\Delta H_f^\circ = \Delta H_{vap}^\circ + \Delta H_{IE}^\circ + \Delta H_{BE}^\circ + \Delta H_{EA}^\circ - \Delta H_{LE}^\circ$

This is the simplest Born-Haber cycle. It is possible for additional terms to be required. For

example, $Cs_{(s)} + I_{2\,(s)}$ also requires a heat of vaporization for the solid iodine. Likewise, $Ca_{(s)} + F_{2\,(g)}$

requires both a 1st and 2nd ionization energies for the calcium and the electron affinity for fluorine

would be multiplied by two because of stoichiometry.

A careful look at the cycle for cesium fluoride yields an interesting (and at first perplexing)

observation: three of the four terms are always endothermic, yet we know heat of formation must be

exothermic. That is, all terms (except electron affinity) always cost energy. You must put in energy

to break a bond, remove an electron from a neutral atom or cation, and move a material into the vapor phase (if it isn't already there). In the case of electron affinity, the second electron affinity of all substances is endothermic, so even this term isn't necessarily favorable for product formation. So, why do ionic compounds form?

The <u>lattice energy</u>, $\Delta H_{LE}°$, is the energy required to completely separate one mole of a solid ionic substance into gas phase ions. Of the quantities in the equation above, we can measure all but lattice energy. That must be determined via a Born-Haber cycle. The resulting equation is:

$$\Delta H_{LE}° = \Delta H_{vap}° + \Delta H_{IE}° + \Delta H_{BE}° + \Delta H_{EA}° - \Delta H_f°$$

As you can see from Figure 7.13 (p. 373) lattice energies are all very endothermic. Why? First, lattice energy is really a measure of the attraction ions have for each other in the solid state. The magnitude of the attraction arises from the construction of the crystal and the nature of ionic interactions.

The simplest crystal pattern to visualize is that of sodium chloride, so we'll use it as an example, but all other patterns work the same way. Consider an isolated sodium ion. All nearby chloride ions will attract it since they each have a negative charge. Unlike in a molecule though, ions do not bind to a specific neighbor, they are attracted to several neighbors, in this case: 6.
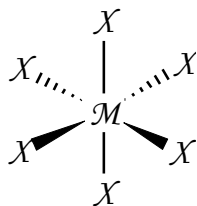
Likewise, each chloride ion is surrounded by and attracted to 6 sodium cations. This explains why it is so difficult to separate an ion from the lattice. The lattice holds each ion in place by strong interactions at several sites.

Since the energy of attraction for any two ions is given by: $E = k\dfrac{Q_1 Q_2}{d}$, *lattice energy increases*

in magnitude as the charges on the ions increase and increases as the ions get smaller (and, hence,

pack closer together).

 We finally should address the question: If increasing charges stabilize the crystal, why don't

we get Cs_2F? Remember it costs a lot of energy to break a noble gas core of electrons. The extra

energy from electrostatic attraction of more highly charged ions never exceeds the energy needed to

remove an electron from the core. Thus, Cs_2F is energetically uphill from CsF. A similar logic applies

to why CsF_2 does not exist.

 Earlier we covered some properties of ionic compounds. We revisit them here with explanations.

1) *Ionic compounds tend to be hard and brittle. Again, this arises from ionic interactions. Let's*

 look at a sodium chloride crystal (Figure 1; dark grey = sodium ion; blue-green = chloride ion)
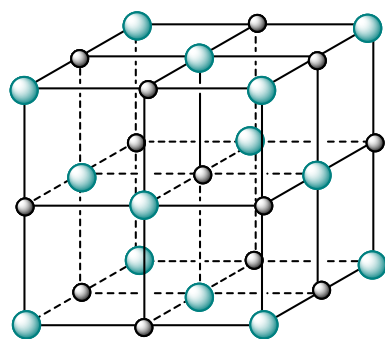
force
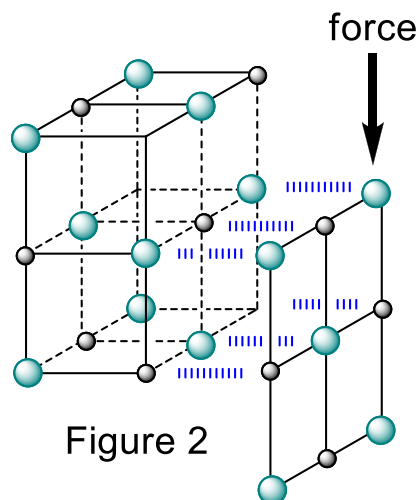
Figure 1

Figure 2

If a mechanical force were to push down on the first vertical sheet of ions, what would happen?

Each ion moves away from a nearby ion of opposite charge and each moves closer to an ion of the

same charge. Thus, simultaneously, attractions decrease and repulsions increase. The result is

that it is very difficult to initiate displacement, but once the crystal face shifts one bond length

it shears off (Figure 2).

2) *Ionic solids conduct electricity poorly, but when melted or dissolved are good electrical conductors. When molten or in solution, ions are free to move and charge can be transported. In a solid lattice, ions are locked into place so there is no way to move charge.*

3) *Ionic compounds have high melting points. Ionic and covalent bonds are both strong, but unlike covalent bonds, ionic bonds are not directed at only one other atom. Instead all anions, particularly those close by, are attracted to a given cation and vice versa. The result is extended arrays of ions that are held strongly together. Thus, in molecules the bonds are all between atoms within that molecule, while in salts the bonds occur between species in adjacent units.*

Compounds with covalent bonds usually have very different properties than ionic compounds. Molecular substances typically are soft and have low melting points. This is because they are discreet units. A comparison of the strength of a typical single bond shows it to be similar to that of a +1/-1 ionic bond. The difference is that the single bond exists between only two atoms, while the charges species interact in all directions. The result is that molecules interact with other molecules through means other than chemical bonding. These forces between molecular are much weaker than chemical bonds and lead to the observed properties.

Evidence for the validity of this argument comes from network covalent substances. These are materials continuously bound by covalent bonds. Diamond and quartz (SiO_2) are examples. Diamond is essentially one giant molecule of carbon and this creates the same sense of hardness one observes for ionic compounds, which likewise have the extended bonding network. Quartz has a similar structure.

7.6 *Molecular Structure and Polarity*

Now we discuss molecular geometry; i.e. the shapes of molecules. This is actually quite important in a lot of chemistry. For example, most enzymes will react with molecules possessing only a certain, specific shape. Small, sometimes seemingly trivial, changes in a molecule may prevent it from interacting with the enzyme. While usually less dramatic with small molecules, the shapes of substances can have a significant impact on their reactions and on their physical properties. For example, two isomers of pentane, C_5H_{12}, are normal pentane ($CH_3CH_2CH_2CH_2CH_3$) which melts at -130 ºC and neopentane ($C(CH_3)_4$) which melts at -16 ºC. This 114 ºC melting point difference arises almost solely from the differences in the shapes of the molecules.

A couple of times earlier in the notes this chapter, the term "bond length" was used without a definition. The definition is what you would probably guess: the distance between two bound nuclei. Similarly, a bond angle *is the angle between any two pairs of bound atoms with a common central atom (i.e. A-B-C, the bond angle would be that with "B" at the vertex).*

VSEPR (Valence Shell Electron-Pair Repulsion) Theory

The system for determining molecular geometries is actually fairly intuitive. First, assume a molecule, **AB**$_n$*, where* **A** *and* **B** *are any two nonmetal p-block elements, all of the* **B** *atoms are bound to the* **A** *(i.e.* **A** *is a "central" atom), and n ≥ 2. Let's also start out assuming* **A** *has no lone pairs of electrons. Where do we place the* **B** *atoms on an imaginary sphere surrounding* **A***? They will try to avoid one another by spreading out across the surface as far from each other as possible. Why? The atoms are so small that bumping into each other is* not *the reason. For now, the best way to think about this is that the electrons (either a bond or lone pair) occupy space and the charges on the electrons repel each other.*

Thus, both bonding and lone pair electrons arrange themselves about the atom so as to minimize interactions with each other. In other words, they spread out as much as possible. This is VSEPR theory (valence shell electron pair repulsion theory).

There are 5 basic shapes or "electron-pair" geometries molecules assume. These pairs of electrons will arrange themselves to minimize contact with each other according to the following table: (# of pairs is the same as the book's "regions of high electron density").

# of pairs	base (e⁻ pair) shape	# of pairs	base (e⁻ pair) shape
2	linear	5	trigonal bipyramidal
3	trigonal planar	6	octahedral
4	tetrahedral		

Pictures of each of these shapes will appear on the following pages. All of the shapes discussed in this section may be found at on the course website in movable format. The bonding and lone pair electrons of almost all molecules will adopt structures based on these 5 shapes. It turns out that not all molecules with 4 pairs of electrons oriented about the central atom will look tetrahedral. Why not? While lone pairs occupy space, they aren't counted when describing the structure. The _molecular geometry_ is the shape of the molecule including only bound atoms. It is the shape you would see if molecules were composed of balls held together by solid rods. If all pairs of electrons are bonding electrons, the molecular shape is the same as the base shape.

In general, use the following rules to determine the shape of a molecule.

1) Draw the correct Lewis structure.

2) Determine the total number of electron pairs around the nucleus in question by adding the number of lone pairs and bonding pairs on the central atom. Count multiple bonds as a single

bonding pair.

3) Use this total to select the base shape from the table above.

4) Place the electron pairs around the atom in the least crowded way. This requires lone pairs go

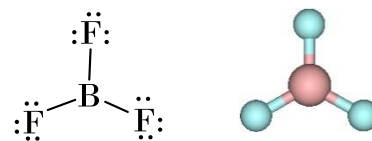into the least hindered positions. Multiple bonds are larger than single bonds.

Rule 4 affects only atoms with 5 or 6 pairs of electrons. We'll now go over some examples.
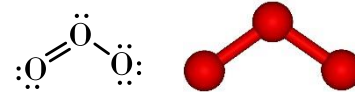
Total electron pairs = 2

The molecule is _linear_ with 2 bonding pairs or one each bonding pair/lone pair.

Total electron pairs = 3: base shape = trigonal planar

bonding prs = 3   _lone pairs_ = 0 ⇒ trigonal planar BF_3

| 2 | 1 | ⇒ bent | O_3 |

| 1 | 2 | ⇒ linear | O_2 |

Total electron pairs = 4: base shape = tetrahedral

bonding prs = 4   _lone pairs_ = 0 ⇒ tetrahedral CH_4
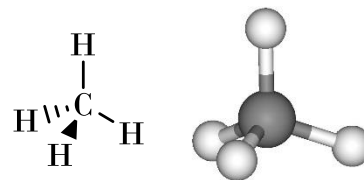
| 3 | 1 | ⇒ trigonal pyramidal NH_3 |

| 2 | 2 | ⇒ bent | H_2O |

| 1 | 3 | ⇒ linear | HF |
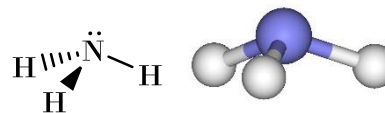
For the next two base geometries, we must consider lone pair placement. The 5 positions on a

trigonal bipyramid are not all equivalent. Those in the axial (A) position are more crowded because

they have 3 x 90° contacts, while those in the equatorial (E) positions have 2 x 90° and 2 x 120°

contacts. Since the 120° positions are swept back, these are very weak interactions and may be ignored. The figures below show the different positions, the 90° interactions, the 180° interactions, and an alternative way of viewing the molecule, respectively. It is important to remember that the last view does not show correct atom connectivity for all atoms, but may make visualizing the molecule easier.
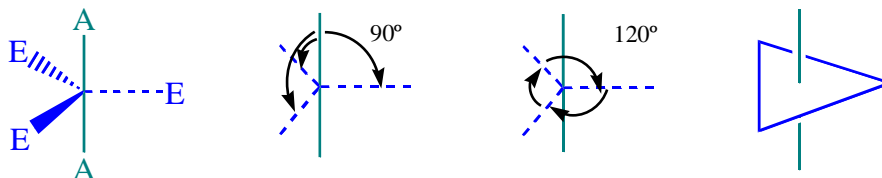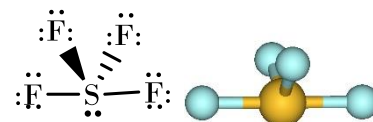

Total electron pairs = 5: base shape = trigonal bipyramidal

bonding prs = 5 lone pairs = 0   ⇒ trigonal bipyramidal PF_5
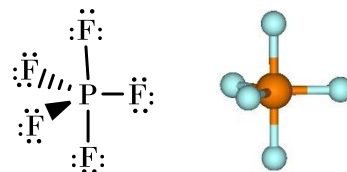
4   1   ⇒ seesaw SF_4

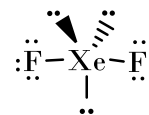3   2   ⇒ T-shaped BrF_3
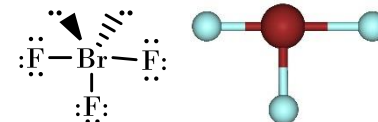

2   3   ⇒ linear XeF_2

In an octahedron, all six sites are initially equivalent. However, after the first lone pair is placed the least hindered position lies opposite to the first lone pair. This is because a position 90° to the first lone pair forces an interaction between the lone pairs that doesn't occur at 180°. Since lone pairs are larger than bonding pairs, placing lone pairs 180° (opposite) to each other is favored. As for the trigonal bipyramid above, the first depiction of the octahedron below shows the correct atom connectivity, while the second may help you visualize an octahedron better.
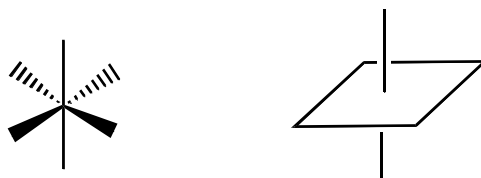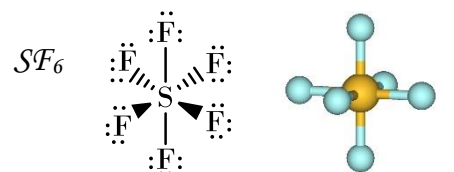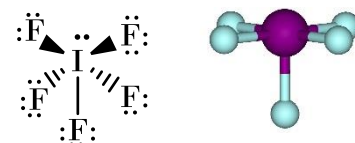
Total electron pairs = 6: base shape = octahedral

Bonding prs = 6   *lone pairs* = 0 ⇒ *octahedral* SF_6

5   *1* ⇒ *square pyramidal* IF_5
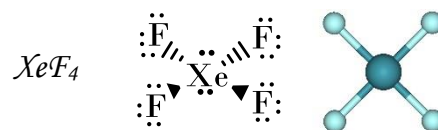
4   *2* ⇒ *square planar* XeF_4

   Finally, one does not normally discuss the "geometry" of a molecule with no central atom (e.g. CH_3CH_2OH); rather the geometry around each atom in the molecule is considered.

Molecular Polarity and Dipole Moment

   Earlier in this chapter, we discussed polar and nonpolar bonds. Remember that in polar bonds the electrons are not shared equally, so a charge separation occurs along the bond.

   A diatomic molecule with a polar bond is also polar. Likewise, diatomic molecules with nonpolar bonds are nonpolar. The centers of positive and negative charge in a polar molecule do not coincide. In the figures below, the arrow points towards the negative charge. The line crossing the arrow makes a "plus" sign indicating the region of positive charge.
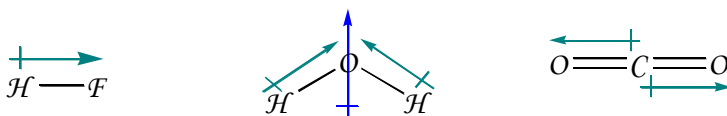
A molecule possessing only nonpolar bonds will always be nonpolar. Molecules containing polar bonds are usually polar, but one must be careful. Treating dipoles as vector quantities is best, however the explanation of that method is involved. I'll use a less mathematical method.

Imagine two atoms of the same element bound together. Their electronegativities are the same so the bond and the molecule are nonpolar. If you think of this as a tug-of-war, with each atom literally pulling on the electron density, you would have a draw. Each atom is equally strong and pulls equally hard. In a diatomic molecule with two different atoms, say H and F, the situation is different. Here fluorine pulls much more strongly than hydrogen (since the former has a higher electronegativity), the electron density shifts towards F and yielding a polar molecule.

Now, consider CO_2 and COS: $:\ddot{O}\!=\!C\!=\!\ddot{O}:$ $:\ddot{O}\!=\!C\!=\!\ddot{S}:$

In CO_2, each bond is polar, but the molecule is linear so the oxygen atoms are pulling equally hard in opposite directions. Thus, even though the bonds are polar, the molecule is not. Like CO_2, COS is linear, but this time the oxygen pulls electrons towards itself more strongly than sulfur (since O is more electronegative than S), so there is a small dipole moment with the negative end towards O and the positive towards S.

In any of the base shapes, if atoms of the same element occupy all positions, the molecule is nonpolar. For others, you must decide if the atoms pulling at the electrons offset or not. If they don't offset, then ask "what is the net direction of the pull?"

January 9, 2023