

Chapter 12 – Chemical Bonding

1) The History of the Development of the Period Table (Not in the book!)

Similarities between the chemical and physical properties of the elements were known early in the nineteenth century. In 1817, Johann W. Döbereiner showed in a number of instances that when three elements with similar properties were listed in order of increasing atomic mass, the middle element had properties that were an approximate average of the other two. His groups of “triads” from top to bottom include:

Li	Ca	N	As	S	Cl
Na	Sr	P	Sb	Se	Br
K	Ba	As	Bi	Te	I

[You might notice that each triad is now a part of a family (or group) of elements in the modern periodic table.]

In 1866, John Newlands established the “Law of Octaves.” Being a lover of music, he theorized that when the elements were arranged in order of increasing atomic mass, every eighth element had similar chemical and physical properties, just like every eighth note on the musical scale has a similar sound! For the lighter elements, this periodicity is surprisingly valid, especially when the noble gases and the transition elements are not considered. He also divided the 56 then known elements and divided them into 11 groups based on characteristics. In 1866, scientists were unaware of the noble gases.

<u>Musical Scale</u>	Do	Re	Mi	Fa	So	La	Ti
Element Scale	Li	Be	B	C	N	O	F
	Na	Mg	Al	Si	P	S	Cl

It remained until 1869 for two scientists, Dmitri Mendeleev from Russia and Lothar Meyer from Germany, to independently establish a periodic table similar to our present-day arrangement of the elements. Mendeleev showed that with the elements arranged in order of increasing atomic mass, their chemical properties occur periodically. When Meyer arranged the elements in order of increasing atomic mass, he found that their physical properties recur periodically. The two tables, however, were virtually identical. Because he drafted his table earlier in 1869, and because he predicted the discovery of other elements and his table included “blanks” for the yet-to-be-discovered elements to fit, Mendeleev is considered the “father of the modern periodic table.”

In 1913, H.G.J. Moseley's study of the X-ray spectra of the elements refined the periodic table to its current status: **when the elements are arranged in order of increasing atomic number, certain chemical and physical properties repeat periodically.**

2) Sec 12.1 – Types of Chemical Bonds

In Chapter 3 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**.

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 11 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 a more useful trend for this chapter is the trend in the **electronegativity**.

3) Sec 12.2 – 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, there is a figure on page 362 that lists the electronegativities for the elements (but not the noble gases!). You can see from this figure that the TREND in electronegativity is inversely related to size – as size gets smaller, the electronegativity increases. Thus, the least electronegative element is Francium (the largest element) and the most electronegative is Fluorine.

a) When the atoms in a molecule are the same, the bonding electrons are shared equally, and the bond is a nonpolar covalent bond.

b) When two different atoms are joined by a covalent bond and the bonding electrons are shared unequally, the bond is called a polar covalent bond. The atom with the stronger electron attraction (the more electronegative atom) in a polar bond acquires a slightly negative charge. The less electronegative atom acquires a slightly positive charge.

c) Electronegative Difference and Bond Types

<u>Electronegative Difference</u>	<u>Type of Bond</u>
0.0 - 0.4	Covalent (nonpolar)
0.4 - 1.0	Covalent (moderately polar)
1.0 - 1.9	Covalent (very polar)
1.9 or more	Ionic (metal and non-metal)

These values are really just averages for where we distinguish between the kinds of bonds. There are, in fact, some ionic bonds where the electronegativity difference is 1.7 and some polar covalent where the difference is 1.9.

Examples

Predict the type of bond that would be found between the following:

a) P and Cl

b) B and H

c) K and Br

4) Sec 12.3 – Bond Polarity and Dipole Moments

a) In a polar molecule, one end of the molecule is slightly negative, and one end is slightly positive. A molecule that has two poles is called a dipolar molecule or a dipole. A molecule that has a center of positive charge and a center of negative charge is said to have a **dipole moment**.

b) The molecular shape of polyatomic molecules (molecules containing more than two atoms) along with the polarity of the covalent bonds determines if the molecule will be polar or nonpolar.

c) Polyatomic molecules with no polar covalent bonds and no unshared electron pairs around the central atom are nonpolar.

d) Polyatomic molecules with the covalent bonds and lone pairs (if present) arranged symmetrically around the central atom are nonpolar. (It does not matter if the covalent bonds are polar.)

e) Polyatomic molecules with polar covalent bonds and/or lone pairs of electrons that are not arranged symmetrically about the central atom are polar.

Examples – Are the neutral molecules below polar or nonpolar?

1) PCl_3

2) SO_2

3) CCl_4

5) Stable Electron Configurations and Charges on Ions

The stability of the noble gas configuration influences the number of electrons that atoms tend to lose or acquire by either transferring or sharing.

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.

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.

6) 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**

- 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.
- Step 3:** Place two electrons in each bond between each pair of bonded atoms.
- 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, H₂O.

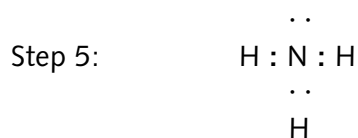
- Step 1: $1 + 1 + 6 = 8$ total valence electrons
- Step 2: H O H
- Step 3: H : O : H
- Step 4: Since the attached atoms are hydrogens, they cannot accept any more electrons (duet rule).
- Step 5: H : $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$: H

Example: The Lewis structure of the ammonia molecule, NH₃.

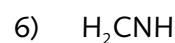
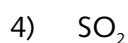
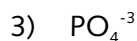
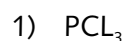
- Step 1: $1 + 1 + 1 + 5 = 8$ total valence electrons
- Step 2: H N H
 H



Step 4: Since the attached atoms are hydrogens, they cannot accept any more electrons.



Examples – Give Lewis Structures for each of the following:



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.

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

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. Two examples of these are NO_2 (17 valence electrons) and BF_3 (an electron deficient molecule).

9) A Summary of Some Other Factors with Lewis Structures

- A coordinate covalent bond is formed when one atom contributes both bonding electrons in a covalent bond. (ex.: ammonium ion)
- 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)
- 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.

10) Sec 12.8 – Molecular Structure

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. Both 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.)

11) Sec 12.9 & 12.10 – 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:

- a) 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.
- b) 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).
- c) Unshared electrons 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.

d) 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 VESPR.

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

