

Chapters 9&10 – Structure and Bonding Theories

Ionic Radii

Ions, just like atoms, follow a periodic trend in their radii. The metal ions in a given period are smaller than the non-metal ions in the same period. This is because the metal ions have lost electrons leaving only the inner shells with electrons. However, the trend across a given period is for the ions to decrease in size in a manner similar to the atoms. The ions will start to decrease in size across the metals. The radius then abruptly increases with the first non-metal and then decreases again from there.

Electron Dot Symbols

A method of gaining understanding of the way in which atoms can bond is to depict the **valence**, or outer shell, electrons around the chemical symbol for an element in a way that shows how many bonds the atom is likely to form. Writing what are known as electron dot symbols for the elements does this. The electrons are placed around the atom on one of each of the four sides. There will be a maximum of 2 electrons per side and the electrons are placed following an analog of Hund's rule: one electron per side until each has one then they are paired up. Following this rule will give us an indication of how many bonds a particular element can form. The electron dot symbol for Hydrogen is the simplest:



Helium would look like:



This doesn't follow the above rule because 2 electrons fill the valence shell for Helium. Carbon would look like:

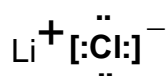


The presence of unpaired electrons is an indication of the number of bonds it is likely to form. Hydrogen is likely to form only one bond. Carbon is likely to form 4 bonds but there are exceptions though. Helium is not likely to form any bonds. This knowledge can help us to decide which atoms are bonded to which other atoms. This means that we can now draw electron dot structures of molecules. **Electron dot structures** (or **Lewis Dot Structures**) are two-dimensional representations of the bonding in molecules. When we have an idea of the bonding that is present in a molecule we can then make decisions about the molecule such as how the atoms are arranged in three-dimensional space and whether or not the molecule is polar.

Electron Dot Structures

An electron dot structure allows us to determine the bonding in a molecule. It will show us which atoms are connected to each other. Once this information is obtained we can use it to determine other properties of the molecule.

The simplest electron dot structures are those for the binary ionic compounds. These are comprised only of the electron dot symbols for the ions. All metals lose electrons to form ions. This is represented by the electron dot symbol for the element without any electrons. We are talking about only the main group elements. For instance, lithium will lose its 1 2s electron to form an ion. It therefore will have no valence electrons to represent in the symbol. All non-metals gain electrons to form ions. This is represented in the electron dot symbol by a completely filled octet of electrons around the atom. When a non-metal gains electrons, it gains enough electrons so that it has the same electron configuration as the nearest noble gas. This means that the valence shell of a non-metal ion will contain eight electrons. The symbol for the non-metal ion will be enclosed in square brackets. This indicates that all of the electrons belong to the ion and none of them are shared. The symbol for the metal ion is placed first with the symbol for the non-metal ion placed next to it.



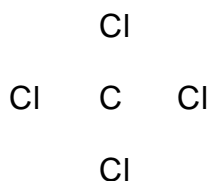
Covalent compounds are almost as easy. To draw the electron dot structure for a covalently bonded compound we have to follow a few rules.

1. Determine the skeletal structure of the compound. This will involve determining the central atom. The central atom is going to be the atom that forms the most number of bonds. If there are two atoms that form the same number of bonds, the atom that is least **electronegative** will be the central atom. All of the other atoms will be arranged around the central atom.
2. Count the number of valence electrons in the compound. If it is a polyatomic ion, add one electron for each negative charge and subtract an electron for each positive charge.
3. Connect all the outer atoms to the central atom by single bonds (use a single line). A single bond is two electrons.
4. Give all of the outer atoms an octet by placing the appropriate number of electron pairs around each atom. Any left over electrons are placed in pairs on the central atom.
5. If the central atom does not have an octet, convert lone pairs on the outer atoms to form double or triple bonds until the central atom has an octet.

Example:

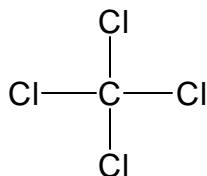


Step one: The central atom is going to be Carbon because it can form the most number of bonds and it is the least electronegative.

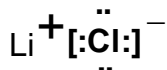
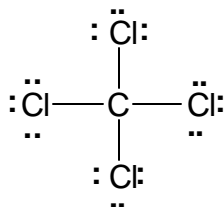


Step two: There are 32 valence electrons.

Step three: Connect the outer atoms to the central atom by single bonds.



Step four: Give the outer atoms octets.



all atoms have octets at this point and there are no more electrons. We are done with this structure.

Not all structures will have an octet on the central atom. Sometimes there are not enough electrons to complete the octet. An example of this is the BF_3 molecule. There are not enough electrons to complete the octet on the Boron. We could draw a double bond between the Boron and one of the Fluorines. This is not correct. We can see why when we calculate **formal charges**. **Formal charges** are hypothetical charges the atoms would have if all of the electrons in the bonds and lone pairs belonged to a particular atom. We can calculate the formal charge by:

Formal charge = # of valence e^- - # of e^- in lone pairs - $\frac{1}{2}$ the # of e^- in bonds.

Some rules for using formal charges:

The sum of the formal charges should equal the charge on the compound or ion.
The structure that contains the most formal charges equal to zero is more likely.
The negative formal charge should be on the most electronegative element.

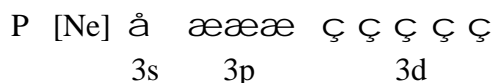
Electronegativity

Electronegativity is the tendency of an atom to attract electrons to it when it is covalently bonded to another atom. The trend of electronegativity in the periodic table is that Fluorine is the most electronegative element and Cesium is the least. As we move away from fluorine in the periodic table, electronegativity decreases.

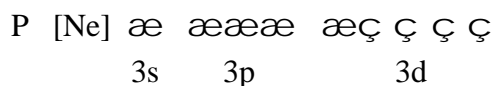
Electronegativity can also be used to determine polarity. We will discuss this aspect of molecules after we can determine the molecular geometry.

Other violations of the “Octet rule”

Elements in period three or higher can violate the octet rule in the other direction. They can have more than eight electrons around the central atom. We can see why this can happen if we look at the orbital diagram of an element from the third period, like Phosphorus:



This is the ground state of Phosphorus. The 3d orbitals are represented but they are empty. If we wish to create more than three bonds around a Phosphorus atom we can promote an electron from the 3s orbital to the 3d:



Using this configuration we can now make up to five bonds (10 electrons) around a Phosphorus atom. Only elements in the third period or higher can do this because only these atoms have the d orbitals available.

Resonance structures

Sometimes we are able to draw more than one correct electron dot structure for a molecule. When we look at formal charges there is no way to distinguish between the two structures. Here is an example:



Both of these structures are correct. When this happens the molecule is said to have **resonance**. Resonance lends stability to a molecule. The two structures above are called **resonance structures**.

Molecular Structure

Once we are able to determine which atoms are bonded to each other and the number of lone pairs on the central atom we can then make a determination about the shape of the molecule. This is done using a model known as **VSEPR**, or **Valence Shell Electron Pair Repulsion**. This model postulates that the electron groups, or pairs, will repel each other and get as far away as they can from each other around the central atom. This results in the molecule having a particular shape. There are two kinds of geometries we can talk about. The first is called the **electron pair geometry**, which shows us how the groups of electrons are arranged around the central atom. The second is called the **molecular geometry**, which shows us how the atoms are arranged in three-dimensional space.

Electron Pair Geometry

There are five kinds of electron pair geometry. This depends solely on the number of groups of electrons around the central atom. We need to remember that multiple bonds (i.e., double and triple bonds) count as one group of electrons. The number of groups of electrons determines the electron pair geometry:

Number of electron groups	Electron Pair Geometry
2	Linear
3	Trigonal Planar
4	Tetrahedral
5	Trigonal Bipyramidal
6	Octahedral

These are the **ONLY** five electron pair geometries. The electron pair geometry leads to the molecular geometry.

Molecular Geometry

Molecular geometry can be derived from the electron pair geometry. If we ignore the lone pairs (but not their effect on the other electron groups) and just look at where the atoms are we are looking at the molecular geometry.

Total e ⁻ groups	# of lone pairs	Electron Pair Geometry	Molecular Geometry
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2	0	Linear	Linear
	1	Linear	Linear
3	0	Trigonal Planar	Trigonal Planar
	1	Trigonal Planar	Bent
4	0	Tetrahedral	Tetrahedral
	1	Tetrahedral	Trigonal Pyramidal
	2	Tetrahedral	Bent
5	0	Trigonal Bipyramidal	Trigonal Bipyramidal
	1	Trigonal Bipyramidal	See-Saw
	2	Trigonal Bipyramidal	T-Shaped
	3	Trigonal Bipyramidal	Linear
6	0	Octahedral	Octahedral
	1	Octahedral	Square Pyramidal
	2	Octahedral	Square Planar

As we can see from the table, the electron pair geometry and the molecular geometry is the same if the number of lone pairs is zero. This makes sense because if there are no lone pairs on the central atom, there is an atom wherever there is an electron group. When there are one or more lone pairs the molecular geometry differs from the electron pair geometry.

Molecular Polarity

Now that we are able to determine the shapes of molecules, we can also determine if the molecule is **polar** or not. A molecule is polar if there is a separation of charge in the molecule. This arises due to the difference in electronegativity in the atoms comprising the molecule. Each bond that is between two atoms of differing electronegativity is polar. The degree of polarity depends on the magnitude of the electronegativity difference.

The polarity of the molecule depends on the arrangement of the polar bonds in space, in other words, the molecular geometry. If the polar bonds are arranged symmetrically around the central atom they will cancel each other out and the molecule will be non-polar. If they are not symmetrically arranged, they will not cancel out and the molecule will be polar.

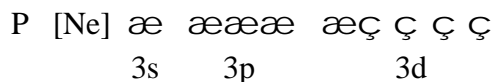
We can determine if they are symmetrically arranged by a simple test. If we rotate the molecule around a bond such that we change the positions of the atoms and the molecule looks the same it is symmetric and therefore it is non-polar. If the molecule looks different, it is polar.

Bonding Theories (Models)

There are two bonding theories that we are going to look at. They are not the only bonding theories and they are by no means complete. They are both models of the way two or more atoms bond. As they are both models, they both leave something of the complete picture out. They both still have their uses. The first theory is called **Valence Bond Theory**. This theory will give us information about the geometry and structure of the molecule. The second theory is called **Molecular Orbital Theory**. This theory is a bit more complicated. It will not easily give us information about the geometry of the molecule but it will give us information about the magnetic properties of the molecule that Valence Bond Theory does not.

Valence Bond Theory (VBT)

VBT is a theory that is based on something we touched on briefly when discussing molecules that have more than an octet around the central atom. We saw that Phosphorus can promote an electron to the d orbital:



This works fine except for the fact that if this were the case we would have three bonds that were the same and 90° away from each other and the other two bonds would be different. We know that the bonds are all the same and that they point toward the corners of a trigonal bipyramid. We can eliminate this problem by mixing or **hybridizing** the orbitals. This will give 5 new orbitals that have the same energy and point in the proper directions.

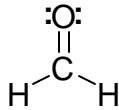


These orbitals are called sp^3d because they are from the hybridization of an s, 3 ps, and a d orbital. If we examine the other types of electron pair geometry we find that the shapes are explained by the hybridization of various combinations of orbitals.

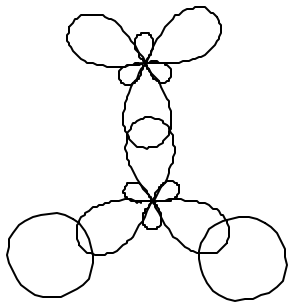
Geometry	Hybridization
Linear	sp
Trigonal Planar	sp^2
Tetrahedral	sp^3
Trigonal Bipyramidal	sp^3d
Octahedral	sp^3d^2

The explanation of Double and Triple bonds

Let's look at the molecule CH_2O which has the following electron dot structure:

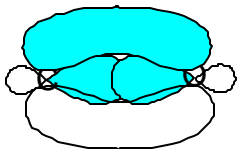


This molecule has trigonal planar geometry. This means that the Carbon atom is sp^2 hybridized. If we look down on the molecule as we see it in the electron dot structure we would see:



Here we see the sp^2 hybrid orbitals on the carbon and the oxygen (propeller shapes). We also see the s orbitals from the Hydrogen atoms (circles). The overlap in the middle of an sp^2 orbital on carbon and an sp^2 orbital on oxygen gives one of the bonds in the double bond.

When we have sp^2 hybridization we have only used two of the available p orbitals. There is still one more left. We can use the p orbitals for bonding purposes also. This is what we would see in the above molecule looking at it in the plane of the molecule:



Here we are ignoring the hydrogens and lone pairs. The curved shapes on the top and bottom are the overlap of the p orbitals on the Carbon and oxygen atoms. These form the second of the bonds in the double bond.

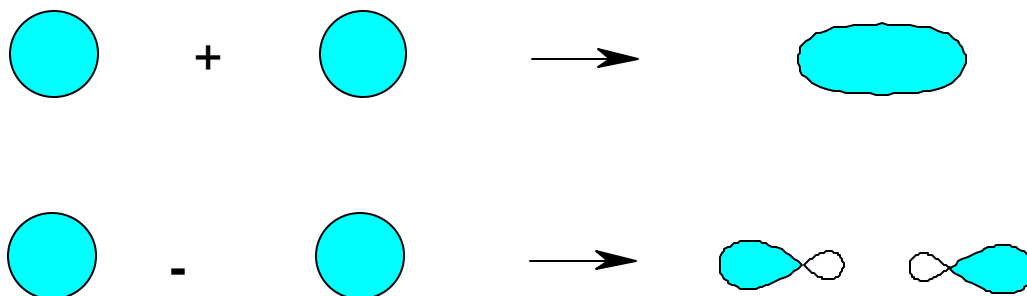
The overlap of sp^2 orbitals in the molecule results in what is known as a $\hat{\sigma}$ bond. The overlap of the p orbitals in the molecule results in what is known as a $\tilde{\pi}$ bond. $\hat{\sigma}$ bonds result from the overlap of orbitals that meet end-to-end. $\tilde{\pi}$ bonds result from the overlap of orbitals that meet side-by-side. In any bond one of the bonds is a $\hat{\sigma}$ bond. The rest are $\tilde{\pi}$ bonds.

A triple bond always gives a linear geometry or sp hybridization. This means that there are 2 p orbitals that can overlap forming 2 $\tilde{\pi}$ bonds. The sp overlap results in a $\hat{\sigma}$ bond. The two $\tilde{\pi}$ bonds will be perpendicular to each other along the axis of the bond.

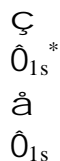
Molecular Orbital Theory (MO)

MO theory takes a different path to explain the bonding in molecules. It starts with the atomic orbitals and linearly combines them to form a new set of orbitals called molecular orbitals. This is not the same thing as the hybridization from VBT. The different kinds of atomic orbitals are in general not mixed.

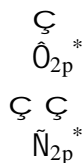
If we start by looking at Hydrogen (H_2) we can get an idea of what is happening here. We have a $1s$ orbital on each atom. There are only two ways of combining these orbitals in a linear manner. We can add them together or subtract them. If we add them together the energy is lowered and we get a bonding molecular orbital. If we subtract them, the energy is increased and we get an anti-bonding orbital.

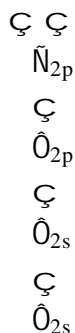


The anti-bonding orbital detracts from the bonding in the molecule. The bonding orbital serves to hold the molecule together. For some of the same reasons as in VBT, the molecular orbital that arises from the end-to-end overlap of atomic orbitals is called a σ orbital. The side-by-side overlap results in a π orbital. The energy level diagram for this molecule will look like:



Here the * designation indicates an anti-bonding orbital. We can expand this idea to the atoms of the second period. The energy level diagram will look like (ignoring the first energy level overlap):





When filling in the energy level diagram we follow Hund's rule just like in atomic orbitals (lowest energies first and one per orbital of the same energy first).

When we look at the molecular orbital energy level diagram we can determine the magnetic properties of the molecule (paramagnetic vs. diamagnetic). If there are unpaired electrons in the diagram the molecule is paramagnetic. O_2 is an example of a paramagnetic compound.

We can also get an idea of the stability of a molecule by calculating the **bond order**. Bond order can be calculated as:

$$\text{Bond order} = \frac{1}{2} (\text{bonding } e^- - \text{anti-bonding } e^-)$$

Higher bond orders indicate more stability.

MO theory also gives a different explanation of resonance. In MO theory resonance is explained as a molecular orbital that encompasses the whole molecule. Instead of being **localized** between two atoms, like in VBT, the electrons are **delocalized**, or spread over the whole molecule.

Bond length and energy

We have seen that there are three kinds of bonds: single, double and triple. These bonds have lengths and energies that correlate with the kind of bond. A single bond is only 1 pair of electrons as a result it has the lowest energy and is the longest bond. A double bond has 2 pairs of electron and so has higher energy and is shorter. The triple bond is the shortest bond and has the highest energy.

We can use a table of bond energies to calculate an approximation to the enthalpy change, ΔH , of a reaction. If we break a bond we have to put energy into it. This is a positive contribution. Making bonds releases energy and is therefore a negative contribution. To calculate the change in enthalpy we add up all the energies for bonds that are broken and subtract the energies for all the bonds that are formed.

$$\Delta H \approx \sum BE(\text{broken}) - \sum BE(\text{made})$$