# Molecules; Bonding and Geometry
# Unit 2

**“Chemistry The Central Science”, Brown, LeMay, Bursten, and Murphy , 11th Edition.**

**Suggested Reading**

**Chapter 2** Sections 2.6-2.8

**Chapter 3** Sections 3.4 and 3.5

**Chapter 7** Sections 7.1-7.5 discuss in class and 7.6-7.8 on own

**Chapter 8** Sections 8.1-8.8

**Chapter 9** Sections 9.1-9.7

**Suggested Problems (Website)**

***Homework posted on the website!!***

**Suggested Problems (Blackboard)**

**Unit 2 Problems**

previous exam questions and great practice

**Suggested Problems (Text)**

**2**.63, 65, and 67.

**3**.21, 27, 31, 33, and 35.

**7**. 5, 35, and 27.

**8**. 7, 9, 11, 13, 15, 17, 29a and b, 31, 32, 33, 35, 39, 43, 47, and 48.

**9**. 15, 26, 35, 51, and 54.

# Molecules; Bonding

## The Periodic Table

**The Periodic Table**

We just discussed electronic configurations; now let's apply this to the Periodic Table.

Let's start with Group 8A, the noble gases. The outer most energy level, shell, has eight electrons filling both the s and p orbitals. These gases were known for many years not to react with anything; however recent studies show the heavier gases do sometimes react with F and O.

The Group 1A and 2 A elements all have their last electrons assigned to s orbitals, and show very similar reactivity to each other.

Group 3A-8A elements all have their last electrons assigned in p orbitals, and also have similar reactivity the each element in the individual columns.

The Group B elements all have electrons in d orbitals and are known as the transition elements, or as the d-transition elements.

The Lanthanides and Actinides are the f-transition elements or also known as the inner transition elements. They start with Cerium (Ce) which has an atomic number of 58.

***The outer most electrons have the greatest influence on the properties of the elements. Adding an electron to the outer most s or p orbital has a dramatic effect on the physical and chemical properties. Adding electrons to the d or f orbitals has a much smaller effect on properties.***

# Molecules; Bonding

## The Periodic Table

**Atomic Radii**

We have just discussed how to predict where the electrons are distributed are the nucleus, let us consider the entire atom's size.

We can't see an atom to measure the diameter and our calculated energy orbitals do not have a definite "edge", thus we do not actually know the size of an individual atom.

However, we can measure the distances of atoms in solids and the lengths of chemical bonds, so the atomic radii can be calculated in many elements.

Atomic radii size decreases from left to right, and bottom to top in the Periodic Table.

Doesn't this seem backwards? We are adding more electrons, but our atom size is getting smaller. Why?

First, let us consider charge attraction and repulsion. The inner most electrons are attracted to the nucleus, but what about the electrons in the outer shells? They "feel" the attraction to the nucleus less because of the counterbalanced repulsion to the inner shell electrons. This is also why the size increases as you move down each column.

As we move from left to right across the table the number of protons increases and "over balances" the charge of the two electrons in the 1s shell.

# Molecules; Bonding

## The Periodic Table

**Ionization Energy**

This is the energy required to remove the most loosely bound electron from a gas atom to form an ion.

These energies increase as we move left to right across the Periodic Table and decrease as we move down each column.

Elements with low ionization energies easily lose electrons to form cations.

**Electron Affinity**

Electron affinity is the energy absorbed when an electron is added to an atom to form an anion.

Elements with negative electron affinities gain electrons easily to form negative ions (anions).

The electron affinities are little harder to predict in the middle metals, but the halogens are always the most negative. The noble gases and the Group 2A elements are all zero.

**Ionic Radii**

Cations are always smaller than the neutral atoms, and conversely anions are always bigger than the neutral atoms.

Isoelectronic species have the same number of protons. For example, $Li^{+1}$ and $Be^{+2}$ are isoelectronic.

# Molecules; Bonding

## The Periodic Table

**Electronegativity**

The electronegativity is the measure of an element to attract electrons to itself when chemical combined (bonded) to another atom.

Elements with high electronegativities often gain electrons to form anions and elements with low electronegativities often lose electrons to form cations.

For the elements, electronegativity increases from left to right across the table and decreases from top to bottom within each group.

# Molecules; Bonding

## Ionic Bonds

**Compounds, Molecules, and Molecular Formulas**

The combination of elements in precise, well defined ratios into a pure substance called a compound.

***Any compound can by decomposed into its individual elements!!***

**Compounds**, a pure substance made up of two or more elements in a fixed ratio.

The Law of Constant Composition, For example, water is 89% oxygen and 11% hydrogen, not matter where it comes from.

The smallest unit of a compound which retains the characteristics of that compound is a **molecule.**

**Molecules** are groups of two or more atoms held together by the forces of chemical bonds. The composition of a molecule is represented by a **molecular formula**.

Let's look at ordinary table salt.

NaCl
sodium chloride

Why do we have salt? Why form? Why is NaCl a stable molecule? We know elemental sodium is a metal, and elemental chlorine is a gas, yet NaCl is a white solid, why?

# Molecules; Bonding

## Ionic Bonds

This molecule is comprised of two different ions.

Remember: **Ions** are atoms or groups of atoms that carry an electrical charge. The two charges, positive and negative attract, so a positive ion and a negative ion attract each other.

So if Na existed as a positive ion and Cl existed as a negative ion, they would attract. This is exactly what happens and that attraction is what we called our **chemical bond.**

$Na^{+}Cl^{-}$

But notice the positions of both elements on the periodic table. There are general trends within the periodic table that we will build on through out the semester, including this one.

What if your positive ion was $Ca^{+2}$, ions aren't limited to + or - -1.

You would need a (-2) element or 2 (-1), thus $CaCl_2$.

***Molecules are always in strict ratios to form neutral species!!***

Molecular formulas tell you the number of ions and the positive ions are always listed first, like NaCl.

# Molecules; Bonding

## Ionic Bonds

**Chemical Bonding**

We have just discussed the forces that hold elements together, now let us discuss the forces that hole molecules together. There are two major classes of bonding, first ionic bonding results from electrostatic interactions among ions. This type of bonding often results from the over net transfer of electrons from one atom to another. Second, covalent bonding results from sharing electrons between atoms.

These bonding classes represent the extremes!! All bonds have some of both bonding characteristics. Just like our elements have different properties due to their outer most electrons, molecules have different properties bases on the type of bonding between the atoms.

# Molecules; Bonding

## Ionic Bonds

### Lewis Dot Formulas

We just learned the ground state electron configurations for elements, these electrons determine the chemical and physical properties of the elements *and* they determine the number and type of chemical bonds they form. We write these electrons as Lewis dot formulas.

Chemical Bonding involves the **valence electrons**, which are usually electrons in the outermost occupied shells.

***We only write the outer most s and p orbital electrons!!***

The transition metals have too many electrons to use this method!!

Let us start with writing Lewis dot formulas for a few elements.

### Ionic Bonding

***Remember that an ion is an atom with a charge!!***

A positively charged ion is A **cation**

A negatively charged atom is An **anion**

***Ionic bonding is the attraction of oppositely charged ions (cations and anions).***

This type of bonding usually results in the formation of a solid like table salt.

# Molecules; Bonding

## Ionic Bonds

***Ionic Bonding results from a complete transfer of at least one electron from one element to another and the resulting ions are held together with electrostatic interactions .***

When the difference in electronegativity between two elements is large, the elements are likely to form an ionic bond.

Let us consider the Group 1A and 7A elements. Let's draw the electronic configurations for one of each.

***If you form ions both atoms are now isoelectronic with a noble gas!!***

Remember the table? The greatest difference in electronegativity is across the table, the greater this difference the more ionic the bond will be.

The energy associated with the attraction between opposite charges in an ionic solid, is called the crystal lattice energy for that solid.

**Simple ions rarely have a charge greater than +3 or -3!!**

# Molecules; Bonding

## Ionic Bonds

Molecular formulas tell you the number of ions and the positive ions are always listed first, like NaCl.

What does that mean for our mole?

1 mole = $6.023 \times 10^{23}$ *particles* and particles can be molecules.

The molecular mass is equal to the masses of each element in the molecule.

NaCl = 22.9898 g/mol(Na) + 35.453g/mol(Cl) = 58 g/mol NaCl

Let's work another problem

# Molecules; Bonding

## Ionic Bonds

**Naming Ionic Compounds**

First, remember the molecular formula is written with the positive ion first. The names follow the same rule. So your name always starts with the positive ion.

For example, NaCl

sodium chloride

If the ion has a +1 charge the name is just the elements name, i.e. sodium chloride.

If the ion has a +2 charge he name is the elements name followed by the charge number, i.e. calcium(II) chloride, for $CaCl_2$.

We haven't learned enough about electrons and chemical bonding for you to predict the ions charges!! So don't worry, just check the chart in your book (pg. 53 and 136).

After distinguishing your positive ion name, you follow with the negative ions name.

$CaCl_2$, calcium(II) chloride

Again, check the chart in the book for the ion names.

Notice all of the negative ion names end in "ide" or "ate"

Finally, let's go from name to formula.

calcium fluoride

# Molecules; Bonding

## Covalent Bonds

**Covalent Bonding**

We just discussed atoms bonding together with a large difference in electronegativity, but we also see atoms bonding together without a big difference in electronegativity. This type of bonding is called **covalent bonding**. The official definition of a covalent bond is when two atoms share one or more *pair* of electrons.

Let us look at what it really means to “share” a pair of electrons. We’ll start with H. Let us draw out the electronic configuration of two hydrogen atoms.

The energy associated with “sharing” a pair of electrons is distance dependant!!

Let us draw this again including the s orbitals for both H atoms.

# Molecules; Bonding

## Covalent Bonds

Other nonmetal atoms also share electrons to form covalent bonds. Most covalent bonds involve sharing 2, 4, or 6 electrons….i.e. 1, 2, or 3 *pairs* of electrons.

The number of pairs shared denotes the type of bond. For 1 pair of shared electrons we call this a single bond (sigma bond), for 2 pairs we call this a double bond ( pi bond) and for 3 pairs we call this a triple bond (pi bond). Sharing pairs of electrons is possible if the orbitals of the single atoms overlap and essentially form a new orbital. This entire theory of bonding is called **valence bond theory**, or more commonly **molecular orbital theory**.

Remember that there is a magic distance between the nuclei of bonded atoms and at that distance the atoms are “more stable”. The statement “more stable” means the energy associated with the single atoms is more than the energy associated with the bonded atoms, there is a specific amount of energy associated with each bond!! This is called the **bond energy**.

# Molecules; Bonding

## Covalent Bonds

Let's take a look at some more complicated molecules, including atoms with shared and unshared electrons.

How do we decide which electrons are shared between which atoms? What is there are more than two atoms?

## Rules and Steps for Lewis Dot Formulas

**In most compounds the elements in each atom achieve the isoelectronic configurations of the closest noble gas**

Figure out which element is the least electronegative, except H.

Hydrogen is always terminal and can only form one bond.

Place the least electronegative atom in the center, this is called the central atom.

Even space the remaining atoms around the central atom, keeping in mind the following guidelines;

- H always only forms one bond, so it should be terminal
- Atoms tend to form (8 – group number) of bonds, so….
- Halogens (Group 7A) usually form one bond
- Oxygen (Group 6A) usually forms 2 bonds
- Nitrogen (Group 5A) usually forms 3 bonds
- Carbon (Group 4A) usually forms 4 bonds
- Boron (Group 3A) usually forms 3 bonds (does not follow the octet rule)
- Beryllium (Group 2A) usually forms two bonds (does not follow the octet rule)
- Lithium (Group 1A) usually forms one bond (mostly ionic bonds though!!)

Non metals can form single, double, or triple bonds.

Oxygen forms single or double bonds.

Add up the total number of electrons needed for each atom to achieve noble gas configuration, N

Add up the total available electrons for each atom, A

Subtract A from N, this is the total number of shared electrons, S

Divide S by 2, this is the total number of electron pairs

Start by placing the shared electrons as single bonds around the central atom

Place any remaining single bonds to atoms not bonded to the central atom

How many bonds do you have? Subtract this from the total (S).

Check the octet rule for each atom, starting with the central atom.

Fill in double or triple bonds where needed

Have all the pairs been used? Check the number of available electrons. Subtract the number of shared electrons from the available electrons (A-S), these “extra” electrons are used to fill in lone pairs.

Fill in the “extra” electrons as pairs around the appropriate atoms.

# Molecules; Bonding

## Covalent Bonds

**Formal Charge**

The **formal charge** is a *hypothetical* charge on an atom in a molecule. This is an extension of the concept of sharing electrons. We must look at the overall total number of electrons being shared in a molecule and *calculate* the formal charge. Here are some rules to follow;

FC = (group number)-[(number of bonds)+(number of unshared electrons)]

**In our Lewis dot formula if an atom has the same number of bonds as its group number it has a FC of zero.**

The sum of the FC in a molecule is always zero!!

In a polyatomic ion, the sum of the FC is the FC.

# Molecules; Bonding

## Covalent Bonds

**Limitations to the Octet Rule**

There are a few elements which do not fill the octet rule.

Be usually only forms two bonds with its two valence electrons.

The Group 3A elements tend to form only three bonds, especially B, and share six instead of eight electrons.

Compounds or ions with an odd number of electrons.

Compounds or ions who need to share more than eight electrons to hold all the available electrons.

These species are usually very reactive!! For example, B forms $BH_3$ and has an empty orbital available. This molecule readily will accept a pair of electrons to share and form an ion, with the formal charge of +1. This makes $BH_3$ a Lewis acid.

# Molecules; Bonding

## Covalent Bonds

**Resonance**

A molecule in which two or more Lewis formulas with the same arrangement of atoms can be drawn is said to exhibit resonance.

This is usually seen with double or triple bonds!! For example, $CO_2$;

Experimentally the CO bond length is between a single and a double bond!! This means the electrons are actually shared between all of these bonds and are **delocalized**, giving a hybrid bond between for all three bonds!!

# Molecules; Bonding

## Covalent Bonds

**Polar and Nonpolar covalent bonds**

Remember covalent bonds are between atoms with similar electronegativities, but not always the same!! This means the electrons being shared may be “pulled” toward ( or attracted to) the more electronegative atoms and not shared entirely equally. This bond is called a polar covalent bond. The term dipolar means “two poles” for us that refers to a positive and negative “pole”.

Let’s look at an extreme case, HF

**Dipole Moments**

We can actually measure the polarity of a molecule, this number is called the dipole moment. The dipole moment has this equation;

In general dipole moments are difficult to measure for each bond in polyatomic molecules and usually reflect the entire molecule. We can write the dipole moments for poly atomic molecules as the sum of the individual dipole moments.

# Molecules; Bonding

## Electronic Geometry

**Covalent Bond Theories**

We have just discussed ( in chapter 7) how to arrange the atoms in a molecule on paper in 2-D using Lewis dot formulas, essentially which atoms are connected to which atoms and with how many bonds. Now let us determine the spatial arrangement of the atoms in 3-D including, the shape and energy of the bonding orbitals. We will rely on two theories and one physical property to determine the shapes and relative energies of these bonding orbitals.

# Molecules; Bonding

## Electronic Geometry

**Valence Shell Electron Pair Repulsion Theory**

This is a general rule for the arrangement of electrons in covalently bonded molecules. The rule states;

Every pair of electrons around the central atom in a molecule will be as far away from the other pairs of electrons as possible.

In simple terms every bond and every lone pair will be placed as far apart as possible around the central atom and still have the orbital overlap necessary for bonding.

The number of atoms bonded to the central atom and the number of lone pairs on the central atom dictate the 3-D orientation of the groups in space.

There are a set of general shapes designated for each number of atoms and lone pairs on each central atom.

# Molecules; Bonding

## Electronic Geometry

**Valence Bond Theory**

The valence bond theory is guideline to explaining how bonding works. We have already discussed that bonding needs to have overlapping orbitals, but what if the orbitals are not in the same energy level? The same shape? Can we still bond atoms together? Yes, we know this it true by all the compounds we have isolated.

***When atoms come together to form molecules the valence orbitals from both atoms*** **hybridize*****, that is they kind of melt together and take on an average shape for all orbitals involved.***

This process is called hybridization and these orbitals are called hybrid orbitals.

We have a system for labeling these orbitals to designate the number and type of orbitals which have hybridized to form the bonding orbitals in molecules. Again, there is a general guideline which associates the shape of the orbital to shape of the molecules.

# Molecules; Bonding

## Electronic Geometry

**Molecular Polarity**

Recall that bonding between atoms with different electronegativities results in a polar bond, this polar bond can lead to a polar molecule and a dipole. We need to examine the polar forces at work in each molecule to determine the overall dipole moments. The molecular geometry is influenced by polarity and therefore we need to add this bit of information to our 3-D models of orbital hybridization.

Individual dipole moments can add and subtract within a molecule, we will use electronic vectors to show this relationship.