

Chapter 8 Bonding: General Concepts

You are now getting a feel for how some elements have different properties than others elements. Now we are going to go one step upward. Let's start combining our elements together to form compounds. Just as understanding the structure of the atom was fundamental to understanding the properties of the elements, understanding the bonds between elements is going to be fundamental to understanding the properties of compounds. For instance you might expect SiO_2 and CO_2 to have similar properties because they are composed of elements from similar places on the periodic table. Yet SiO_2 is silica (sand and glass) and CO_2 is carbon dioxide, a gas. C with one kind of bonding is the lead in your pencil, C with a different bonding is the diamond you use as an engagement ring. So bonding is important.

8.1 Types of Chemical Bonds

We are already familiar with two types of chemical bonds, the **ionic bond** that forms between metals and non metals, and the **covalent bond** that forms between nonmetals. These are two bonding methods are quite different form each other so let's study the details of each.

Ionic Bonding

Ionic bonding forms between ions of opposite charge (+ and -). The charged atoms or molecules are associated by the Electronic attraction between the two, oppositely charged species.

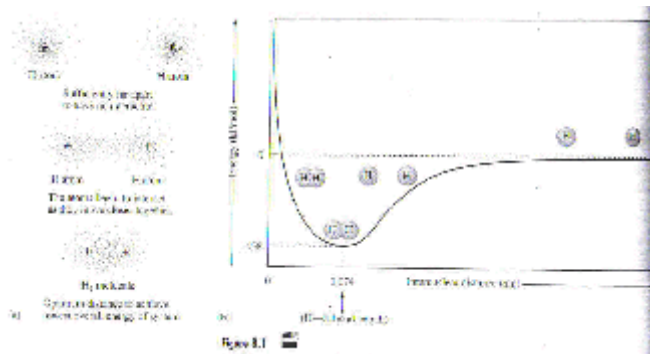
This energy can be calculated using Coulomb's Law

$$E = 2.31 \times 10^{-19} \text{ J nm } (Q_1 Q_2) / r$$

When Q_1 has a different sign than Q_2 you have a negative energy, saying that the force between opposite changes is attractive, so your + 's like to stick to your - 's, This makes for very stable compounds. For instance NaCl melts at 800°C . (Yet, in the proper polar environment like water, these charge attractions are easily ripped apart, and NaCl dissolves readily into the component ions.)

Covalent Bonding

We have just seen that ionic bonding can be understood because the component atoms are oppositely charged. What happens in compounds when they have the same charge?



Let's start with two H atoms at infinite separation. When they are infinitely separate, they don't interact with each other, so we will call this the zero energy level.

As we bring them closer together, we find that the energy of the system gets lower and lower, and then shoots up

when they get very close.

The energy initially gets lower because the electrons between the atoms tend to cluster between the two nuclei so they don't have as much steric repulsion. The energy shoots up when they are close because you have gotten the electrons so close together that they now repel each other

You know from our thermo section that states of lower energy are favored, so 2 H atoms prefer to be in this dip at 0.074nm apart, with **both** of their electrons occupying the space between the atoms.

This sharing of electrons and creation of a low energy state is our covalent bond.

DEF: A covalent bond occurs when two nuclei share one or more valence electrons between them to lower the total energy of the system.

Polarity in covalent bonds

In the covalent bond between H, the two nuclei are exactly the same so they share electrons exactly equally. We know that different nuclei have different attractions for electrons, so often, when the nuclei are different the electrons are not shared equally between them. In this case we have a **polar covalent bond**. A good example is HF. Here you know that F strongly attracts electrons, so you would guess that F would try to pull the electrons to itself. You are right. Thus, we have

HF

$\delta^+\delta^-$ to denote the partial charge on the molecule

The polar bonds have several important properties, one of which is that they are stronger than nonpolar covalent bonds. Can you see why?

When you have a polar covalent bond, not only do you have electrons holding the atoms together, but one atom is slightly positive, while the other atom is slightly negative. This gives you an additional favorable charge/charge interaction that increases the strength of the bonding between the atoms.

The polarity of the bond due to this unequal sharing is very important to the nature of covalent compounds, so let's study it more closely

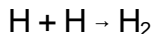
8.2 Electronegativity

Electronegativity is defined as the ability of an atom in a covalent bond to attract shared electrons to itself.

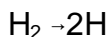
The way we measure electronegativity was developed by Linus Pauling based on the following logic. We assume that all atoms have a certain inherent 'pull' or attraction for electrons in a covalent bond and we call this the atom's electronegativity. Some atoms have a stronger electronegativity or 'pull' while others are weaker. When we have a bond

between two atoms with the same electronegativity they two atoms pull equally, and we have a simple, non-polar covalent bond. When you have two atoms bonded together that have unequal electronegativities or 'pulls' you have a polar bond that is going to be stronger than a non-polar covalent bond. In fact, the greater the difference in the electronegativities of the two atoms, the more polar and stronger the bond will be.

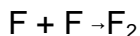
How do we measure the energy of a bond? Simple thermodynamics. Determine the heat released by the reaction



or see how much energy it takes to do the reaction



Let's do a second experiment with F_2 , and see how much E is released when



Now we know the bond strength of H-H or F-F

Now let's look at a compound like H-F

If the HF bond is not electronegative, then we would guess that its E is the average of the H-H energy and the F-F energy.

Now we do the experiment $\text{H} + \text{F} \rightarrow \text{HF}$, and find that this releases MORE energy than expected, so the bond must have added strength from being polar.

Now we do this for all the different elements, and rank them against each other. People have assigned Li as 1 and evaluated all the elements, the results are shown in [Figure 8.3 Electronegativity](#)

As you can see highest electronegativity is at upper right F, and the lowest is at lower left Fr. As with many of our other properties increase in left to right =decrease in up to down

How do we use this? We can predict the polarities of covalent bonds by comparing the electronegativity of the atoms in the bonds. The easiest way is to take the difference between the two values.

'Bond Polarity' = Largest electronegativity - smallest electronegativity

How does the polarity of a C-C bond compare to that of a C-H bond, an NH bond, an OH bond?

$$\text{CC} = 2.5 - 2.5 = 0 \text{ Least Polar}$$

$$\text{CH} = 2.5 - 2.1 = .4$$

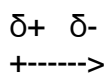
$$\text{NH} = 3.0 - 2.1 = .9$$

$$\text{OH} = 3.5 - 2.1 = 1.4 \text{ Most Polar}$$

Both NH and OH are considered polar, CH is nonpolar, so division is between .4 and .9

8.3 Bond Polarity and Dipole Moments (Bond polarity vs. Molecular Polarity)

When you have a polar bonds and an unequal distribution of charges in a molecule the molecule is said to be **dipolar** or to contain a **dipole moment**. This is often represented as an arrow with a cross, The cross being the + region and the arrow tip being the negative region.



Any diatomic molecule with polar bonds will have a dipole moment. But this isn't necessarily true for other compounds with more than two atoms.

Let's look at H₂O, NH₃, and CO₂

First, where is the + and the negative

H has lower electronegativity than C or N so H is +, N and O are neg

Now look at 3D structure.

In both NH₃ and H₂O, the dipoles are not distributed evenly around the central atom so there is a net dipole within the entire molecule, and it will orient in an electric field. CO₂ on the other hand, has the structure O=C=O and the two dipoles are directed away from each other so the dipole oppose and, **no net dipole**

Other compounds with polar bond but no dipole moment are SO₃ and CCl₄

Bottom line: You can tell if a BOND is polar by looking at the difference in electronegativities of the atoms in the bond. You tell if a MOLECULE is polar by seeing if it has polar bonds arranged in an asymmetric manner.

IONIC BONDING THE DETAILS

8.4 Ions: Electron Configuration and Sizes

Now let's look at ion state for a while

The quantum mechanical models that explain the periodic table also help explain the configuration of atoms in compounds. In virtually every stable compound, the atoms have arranged their electron so they resemble that of a stable gas.

Non metals do this by sharing electrons with other nonmetals, in covalent bonds or by stealing electrons from metals in ionic bonds. Here the metals become cations (+), and the nonmetals become anions (-)

In detail when 2 nonmetals bind in a covalent bond, they share electrons in a way that completes the valence electrons shells of both atoms.

When a metal and a non-metal react to form a binary ionic compound, the nonmetal achieves the valence electron configuration of the next large noble gas, while the valence

orbitals of the metal are emptied to go to the electron configuration of the next smaller noble gas.

Example

NaCl

Na [Ne]3s¹ Cl [Ne]3s²3p⁵

In NaCl

Na=[Ne] Cl=[Ar]

Predicting Formulas of Ionic Compounds

What is an **ionic Compound**?

-usually refers to the **solid state**. A large collection of ions formed in a manner to optimize charge-charge interactions (both favorable and unfavorable)

Some ions like O²⁻ may not exist in gas or water, but will exist in ionic solids where charge matrix stabilized is MgO. In fact most of this section will refer to **solids**

Let's start with the MgO example the electronic configuration of Mg is

[Ne]3s²

and O is

[He]2s² 2p⁴

Oxygen is very electronegative and the large difference in electronegativities means that electrons will transfer from Mg to O

Mg will lose two electrons to go to the [Ne] configuration (Mg²⁺) and O will gain two electrons to go to [Ne] as well (O²⁻)

Note the final ionic compound is electrically neutral and we have predicted the structure of MgO!

So what atoms will take on the configuration of [He] ? H⁻, Li⁺, and Be²⁺

[Ne] ? Na⁺, Mg²⁺, Al³⁺, O²⁻, F⁻

You can figure out Ar, Kr, Xe (see also table 8.3 in text)

This leads to our general rules that

Family	electrons	Charge
1A	-1	+1
2A	-2	+2
3A	-3	+3
4A	-4	+4 (Metals)
5A	-5	+5 (Metals)
6A	+2	-2
7A	+1	-1

a few exceptions

Sn (+2 and +4), Pb (+2 and +4) Bi (+3 and +5) Tl (+1 and 3+)

No simple explanation - for now memorize

Transition metals are even more complicated - valence electrons not well defined

Sizes of Ions

Figure 8.7 of text

Size play an important role in structure and stability of ion

How measure? From distances between ions in ionic solids. However lots of disagreement on how to do this. So look at general trends, not exact values

+ ion usually smaller than parent atom because remove electrons

- ions usually larger than parent because added electrons

Also varies with position on table. Size goes UP as go down (Makes sense adding lots of E-.) Going across the table is complicated. Have metals and nonmetals to compare!

Let's look at **isoelectronic ions** (ions with the same # of electrons)

As number of protons increases, size decreases. More charge to pull closer to the nucleus.

Example

Compare the sizes of the following ions: O^{2-} , Cl^- , Ne, K^+ , Mg^{+2} and Ca^{+2} ?

First the overall ranking

O^{2-} , Ne, and Na^+ are all isoionic

Cl^- , K^+ and Ca^{+2} are isoionic and larger

And I have them ordered from larger to smaller withing each ion so overall:

Smallest

Largest

Na^+ , Ne, O^{2-} , Ca^{+2} , K^+ , Cl^-

8.5 Formation of Binary Ionic Compounds

Now let's talk about the energy that goes in to making an ionic compound. In this discussion will be talking about SOLIDS ONLY. Why?

1. In solids have a crystalline array of + and - that hold together
2. These forces are lost in solution because water pulls + and - ions apart

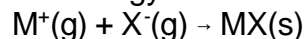
We now understand that ionic compounds are stable for two reasons

1. Each ion has electrons in the noble gas configuration so happy
2. Charge-Charge interaction in crystal should be favorable

Let's see if we can get a handle on this last energy term, the charge-charge

interaction in the crystal. We measure how strongly ions hold on to each other in the solid state by a parameter called the **lattice energy**.

The lattice energy is the energy for the reaction

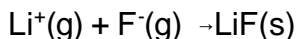


i.e. the change in energy that occurs when two gaseous ions are packed together to form an ionic solid

For ionic solids this should be energy released so what is the sign? (Negative)

In principle calculating a lattice energy is a simple extension of the things we were doing in chapter 9 thermochemistry, simply adding up the E's of several different steps. The tricky part is in getting all the right steps. **Note: I'm going to do this differently than the book.**

What we want is the lattice energy for the reaction



Starting point on board what we want

But what we can measure easily in our calorimeter is



Next point on board what we have

Notice that lots of things have happened in this reaction, We have gone from gas to solid, and atoms to ions as well as making out lattice interaction, so we have to separate out all the other energies

How do we get from one to the other?

Well let's start by changing Li from a solid to a gas What is this (Sublimation can look up value



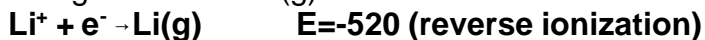
We need the reverse of this reaction to cancel Li(s) from our starting point hence:



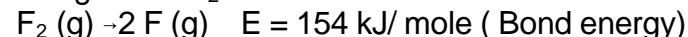
Now that we are in the gas state we need to ionize the gas



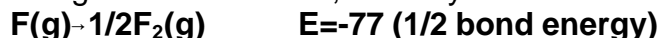
Reverse to get to cancel Li(g)



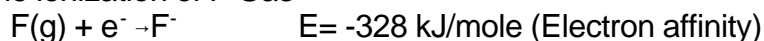
How do we go from F₂ to F? Break a covalent bond



Reverse to get terms to cancel, use only 1/2 because only use 1/2 if F₂



Now the ionization of F Gas



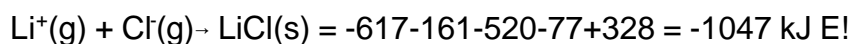
Reverse



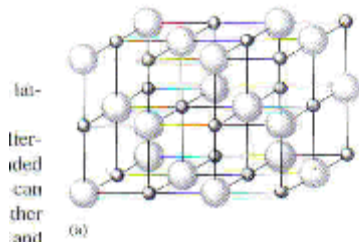
Sum it all up



Total



We get lots of energy from this reaction. Note that the energy we would get by turning F into an ion (-328 kJ) is **less** than the energy it takes to turn Li into an ion (+520 kJ) Thus the transfer of electrons **does not favor this reaction!**



It is the lattice energy gained by putting these ions into the matrix that gives us all the energy!

The lattice formed here is a cubic lattice called the **sodium chloride structure** because this is the most common substance with this form (model for show) All alkali metals and halogen have this structure except cesium salts

lattice energy calculations

The lattice energy can be calculated more directly using a modified form of Coulomb's law

$$Lattice \ energy = k \left(\frac{Q_1 Q_2}{r} \right)$$

Where K is a constant, Q 's are the charges on the ions and r is the distance between them. The equation itself is not important, but look at what it says:

1. The ions have to be opposite in charge for favorable energy

2. The bigger the charge the bigger the energy
3. the smaller the distance the bigger the energy

If we compare the lattice energy of MgO (+2, -2) (-3916kJ/mol) with NaF (+1, -1) (-923 kJ/mol) we see a whopping increase in lattice energy due to the charge effect. This more than compensates for the fact that it takes more energy to produce the doubly ionized state of Mg and O

Now, predict which has a larger lattice E, NaF or KCl
(All +1 charge so that isn't it, $K > Na$, $Cl > F$ so r is larger if R is larger, $1/r$ is smaller so lower lattice E)

8.6 Partial Ionic Character of Covalent bonds Figure 8.12

Now that we have acknowledged that covalent bonds have some ionic character, Now we will confess that all ionic bonds have some covalent character!

In the gas phase we can calculate how the bond between atoms should act for a pure ionic bond, and we find that the actual bond observed in the gas phase always has some covalent character. NaCl and KCl are about 75% ionic while LiF is about the best at 85% ionic. Presumably this has to do with the fact that the gas phase is different from the solid phase, and that the multiple charge interactions of the solid phase give the bonds in this phase a more ionic character.

Things also get messy in that many time our ions contain multiple atoms like NH_4^+ or SO_4^{2-}

Thus NH_4Cl is an ionic compound that contains covalently bound atoms!

COVALENT BONDING - THE DETAILS

8.7 The Covalent Chemical Bond: a model

What? Covalent bonds are Forces that make a group of atoms behave as a unit

Why? Nature likes things at their lowest energy states. Bonds occur spontaneously as groups of atoms achieve their lowest energy.

For sticklers' to the sign convention, please note the following: we are going to use a + sign for a bond energy, hence this represents the Energy we have to add to the system to break or destroy a covalent bond.

For example it takes 1652 kJ of E to change CH_4 back to its elements C and H. Since we have to add energy to do this, it tells you that CH_4 is the more stable arrangement of these atoms. We tend to think of this energy as being localized to the individual bonds.

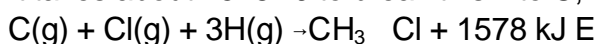
We know that CH_4 has the following structure

C in the center of a tetrahedron, with H's sticking out

Since this is symmetric, the H's are all interchangeable, and equivalent so all bonds are equal in strength and E of the C-H bond is then $+1652/4 = +413$ kJ

Methyl Chloride (Replace 1 H with a Cl)

It takes about 1578 kJ to break this into C, H and Cl thus



Now we will assume that the CH bond in CH_3Cl has the same E as the CH in CH_4 , so our E should be

$$1 \text{ C-Cl} + 3 \text{ CH} = 1578$$

$$\text{CH from } \text{CH}_4 = 1652/4 = 413$$

$$\text{So } 1 \text{ C-Cl} + 3(413) = 1578$$

$$\text{C-Cl} = 1578 - 3(413) = 339 \text{ kJ/mole}$$

So one way of thinking of a bond, is a way to account for the energy that is stored in making a compound from its individual atoms.

Models. A word of caution

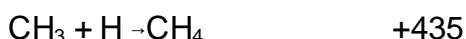
The rest of this chapter will be devoted to developing a model of atomic bonding. You need to remember that this is a model, an invention made to see if we can predict how molecules work. It is NOT the answer, and may eventually be proven wrong. For now the model, with appropriate patches works reasonably well, and helps us to explain much of how molecules react.

8.8 Covalent Bond energies and Chemical Reactions

The bond energies of many different compounds have been analyzed and are shown in table 8.4

Table 8.4

The first thing to remember in such a table is that the reported values are average values, and may vary from one bond to the next depending on environment. For instance, let's see what happens if we break methane down in a series of steps



$$\text{Sum} = +1652, \text{ avg} = +413$$

We can see that the energy of the CH bond varied depending on where it came from or what its environment was. So the first thing you need to remember is that table 8.4 represents average values, and individual values may vary depending on environment

The only bonds we have talked about up to now are where a single pair of electrons is shared between two atoms. This is called a **single** bond. Now we will talk about bonds where 2 and 3 pairs of electrons are shared. These are called **double** and **triple bonds**. (Also given in table 8.4)

The energy of these bonds also varies with length. In general the bond length (distance between atoms) **decreases** as energy **increases** as we go from single to double to triple (see table 8.5)

Bond Energy and Enthalpy

The approach taken in the book here is a bit confusing. I'm going to try a different way.

Once we have tabulated bond energies, we can use these energies to estimate the energies of reactants and products in any reaction, and from there we have yet another way to come up with the energy of a reaction. However things can get a little confusing if you don't pay attention to some of the details. As a result I will take a different approach than the book, to try to avoid some potential problems.

As we have seen in the chapter on thermodynamics, we typically use the equation: $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

This gets a little confusing when applied to bond energies, because we have defined Bond energy = the + E required to destroy a bond. However $\Delta H_{\text{products}}$ or $\Delta H_{\text{reactants}}$ represents the - energy that is released from the compound when its covalent bonds are formed. The sense here is just the OPPOSITE of the bond energy. Hence we will have to put in an appropriate sign change.

So:

$$\begin{aligned}\Delta H_{\text{products}} &= -1 \times (\text{Sum of all bonds in the products}) \\ \Delta H_{\text{reactants}} &= -1 \times (\text{Sum of all the bonds in the reactants})\end{aligned}$$

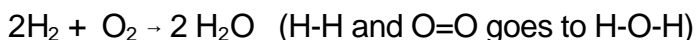
And

$$\Delta H_{\text{rxn}} = [-1 \times (\text{Sum of all bonds in products})] - [-1 \times (\text{Sum of all bonds in reactants})]$$

Note, if you follow everything through you get the same equation as the book

$$\Delta H_{\text{rxn}} = \text{Sum of bonds broken} - \text{sum of bonds formed}$$

Let's demonstrate this with a reaction that we know released lots' of energy, the combination of oxygen and hydrogen to form water.



As I present it:

$$\begin{aligned}\Delta H_{\text{rxn}} &= [-1 \times (\text{Sum of all bonds in products})] - \\ &\quad [-1 \times (\text{Sum of all bonds in reactants})] \\ &= [-1 \times (4 \text{ O-H})] - [-1 \times (2 \text{ H-H} + 1 \text{ O=O})] \\ &= [-1 \times (4 \times 467)] - [-1 \times (2 \times 432) + 1 \times (495)] \\ &= -1868 + 1359 = -509 \text{ for 2 moles of H}_2\text{O or } -254.5 \text{ kJ/1 mole water}\end{aligned}$$

As the book does it, we have to break the covalent bond between 2 H₂ molecules and 1 O₂ molecule, and use this energy to form 4 OH bonds.

$$= 2 \text{ mole} \times 432_{\text{H-H bond}} + 1 \text{ mole} \times 495_{\text{O=O bond}} - 2 \times 2 \text{ mole} \times 467_{\text{O-H Bond}}$$

$$= 864 + 495 - 1868 = -509 \text{ kJ/2 mole H}_2\text{O} = \underline{-254.5 \text{ kJ/1 mole H}_2\text{O}}$$

Do it either way, whatever works best for you.

8.9 Localized Electron Bonding Model -an Overview

So now we have a model for bonding that allows us to account for bond polarity and bond strength. Let's add more details to our model that tells us the actual positions of the electrons in our bond. This is called the **localized electron model (LE)**

In this model we are going to make several assumptions

1. A molecule is composed of atoms that are bound together by sharing pairs of electrons
2. The position of these shared electrons can be specified using the atomic orbitals that you already know
3. Electron pairs are assumed to be localized to a single atom (**Called a lone pair**) or to the space between two atoms (**Called a bonding pair**)

We now need to explore what this model tells us about bonding. There are three different ways that we can explore this model

1. Understanding molecules through the valence electrons and Lewis structures (Section 8.10 -8.12)
2. Predict the geometry of molecules using VSEPR (valence shell electron repulsion model) (8.13)
3. Describe the orbitals used in the molecules based on atomic orbitals (chapter 9)

Let's start with LEWIS Structures

8.10 Lewis Structures Handout - Lewis Rules- end of chapter

Lewis structures are named after G.N. Lewis, and are a way of representing the valence electrons in atoms and molecules (Remember what valence electrons are?)

One of the most important ideas that we have found in exploring chemistry is that *the most important requirement for the formation of a stable compound is that the atoms get to a noble gas electron configuration*

For instance we know that K goes to K⁺ and Ca goes to Ca²⁺ because they are shedding electrons to go to the electron configuration of Ar. Similarly Cl⁻ acquires an electron for the same reason

In a **Lewis structure** we will represent the valence electrons of an atom as dots located around the symbol of an atom. We will show only the valence electrons of an atoms.

Let's try for the Lewis structure of HF



F normally has 7 valence electrons, H has one for a total of 8 electrons. Each dot represents an electron.

We have made the structure with 8 electrons around the F, so its valence shell is filled, and 2 electrons around H, so its 1s valence shell is filled, so both atoms are 'happy'.

There are some other details. As we have seen, electrons like to be in pairs, so we have kept electrons grouped as pairs. One pair is shared between the H and the F so called a **bonding pair**. The three pairs of electrons around the F that are not involved in bonding are called **lone pairs**

In doing these manipulations we need to keep in mind the number of electrons in the noble gas configuration we are trying to achieve. That is, how many valence electrons are there in He (2) Ne(8) and Ar (8). If start working with elements in the 4th period where we go to Kr, we have lots of the transition metals have lots of d electrons that we don't really count as valence electrons, so things get messy, so we will restrict ourselves to just the first 3 periods, or, if we have an element from a higher period we will use just the 1A thru 8A families and ignore the transition metals

Some other examples

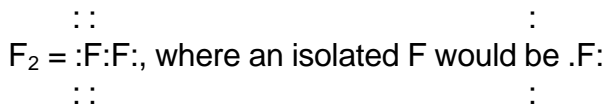
The simplest molecule with a covalent bond is H₂

or

H. + H. Goes to H:H

Note that because H is a 1st period element, so it can only go to a single pair of electrons (called the duet rule)

Let's try something in the second row



Here you can clearly see the electron pair shared between the atoms and how both atoms now have satisfied octets since they want to fill to the level of Ne

Note in this representation we have 3 pairs of electrons that are not shared - these are our **lone pairs** while we have one pair that is shared hence is our **bonding pair**.

Why don't He and Ne form bond? Outer shell filled

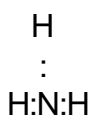
Working with these simple examples is easy, but what about more complicated molecules? In this case resort to the following rules: (also apply in simple case)

- 1. Sum all valence electrons keep track of total, NOT who comes from where
- 2. Use electron pairs to form bonds between each pair of bound atoms
- 3. Arrange remaining electrons to satisfy duet rule for H and octet rule for second row elements

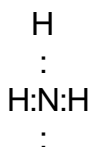
Let's apply this to something complicated NH_3

Total valence electrons? $5 + 3(1) = 8$

Put pairs into bonds

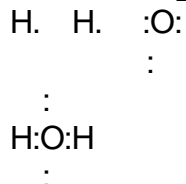


Add remaining electrons to satisfy duet and octet rules



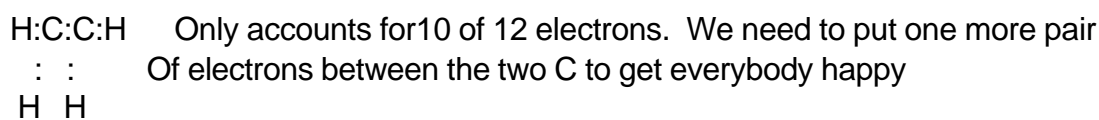
So we can see ammonia will have 3 pairs of bonding electrons shared between the N and the H's and one lone pair of electrons held by the N.

How about water H₂O

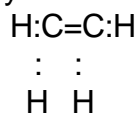


Some compounds have multiple bonds between atoms, for instance C₂H₄

$$\text{Total} = 4(2) + 1(4) = 12$$



When you have multiple bonding pairs, these are written as dashes



You can have triple bonds as well. Let's try O₂ and N₂

O₂ 6 electrons / atom for a total of 12 electrons



N₂ 5 electrons/atom for a total of 10 electrons



Note on multiple bonds. In general only use if at least 1 atom in pair is C, N, or O. These are usually the only elements that use multiple bonds

Also, if you are dealing with ions you can add or remove electrons accordingly thus

NO₃⁻ would have 5 + 3(6) + 1 electrons, you work out the structure

24 electrons



:O:N=O: with a net -1 charge **Note not exactly right - see resonance**



Section 8.12

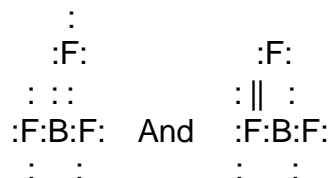
Other examples N≡N, O=O

8.11 Exceptions to the octet rule (rule 8)

As with all simple models there are a few exceptions to the general rules. Let's examine some of those

1. Boron

Several Boron molecules exist where B hasn't fully filled its octet. One of these compounds is BF_3 . We can propose 2 structures for BF_3



The first doesn't look like a good structure because the B needs another pair of electrons. The second looks more reasonable from electron count, but I just said to avoid double bonds if an atom isn't N, C, or O, so which is correct?

Experimentally BF_3 reacts like it wants another pair of electrons. It reacts strongly with compounds like NH_3 and H_2O that have pair of electrons to donate. Thus, experimentally the evidence supports the 1st of the two forms. Other highly reactive electron deficient boron compounds also exist, so always watch out for boron.

Also Be and Al may sometimes have less than an octet

2. Elements in the 3rd period may exceed the octet limit (rule 7)

We know that elements in the third period have 3d orbitals available to them, although they aren't always used. Thus a molecule like SF_6 exist. Here we have a total of $6 + 6(7)$ or 48 electrons. The only way we can make this molecule work is if we have 6 shared pairs of electrons with the S, not the 4 we would expect using the octet rule. We assume that sulfur is used its 3d orbital to hold these extra electron pairs.

Another nasty example is I_3^-

This should have $7(3) + 1$ or 22 electrons

The simplest model would be

$\text{:} \text{:} \text{:}$

:I:I:I: which would only require 20 electrons, thus we have to put 1 more

$\text{:} \text{:} \text{:}$ Electrons pair some place.

As a general rule, when it is necessary to exceed the octet for 3rd or higher row elements, assume the extra electrons are placed on the central atoms (part 2 of rule 7)

```

:::
:!:!: which would only require 20 electrons, thus we have to put 1 more
:::   Electrons pair some place.

```

Let's try 1 more. While I have said in the past that the noble gases are non-reactive, Radon (6th period) can react with Cl to form RnCl₂

Electrons $8 + 2(7) = 22$

```

          : : :
Simplest model :Cl:Rn:Cl: but this has only 20 electrons, so we need to add a pair
          : : :   To the central Rn atom

```

8.12 Resonance

Sometimes you can find more than 1 valid Lewis structure for the compound you are dealing with. Take for example the NO₃⁻ we did earlier

```

      :   24 electrons
      :O:
      : :
:O:N=O: with a net -1 charge
      :   :

```

Use []↔[]↔[] formalism

Notice that I had the double bond to the left and the single bonds up and to the right. Any reason I can't switch these?

So double bond could be in any one of three positions

Now another fact. How can you tell double bonds form single bond?

(More energy, shorter distance)

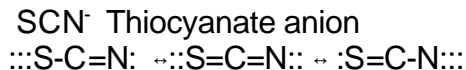
If look at NO₃⁻ find 3 bonds of equal length, intermediate between single and double bonds in length.

The actual answer here is that none of these three structures is itself correct, but that the true structure is an average or superposition of all three.

Resonance occurs when more than one valid Lewis structure can be written for a particular molecule. We usually write double headed arrows between these structure.

This is to indicate not that the true structure is flipping from one form to the next, but that it is a simultaneous average of all the resonance state.

Example 2:



Formal Charge

As you can see above, once we start finding resonance structures, we often find more than one possible non-equivalent Lewis structure. How do we decide whether these are all resonance structure, or if some are better than others?

To do this we need to evaluate the **formal charge** on each atom.

Formal charge = # valence electrons in free atom - # electrons assigned to atom in structure

The formal charge we are going to work with here **is different from** the oxidation state on the atoms we worked with last quarter.

- In Redox bookkeeping we assigned both electrons in a shared pair to the more electronegative atom.
- In Formal charge calculations we will give one electron from a shared pair to each atom
- The second rule is that we will give both electrons in a lone pair to the atoms containing the lone pair.

The idea is that we will go through a Lewis structure and assign a formal charge to each atom. When we compare different structures, the one where most of the atoms have a formal charge of 0 and only the most electronegative atoms have negative formal charges are the best structures.

So let's look at the 3 SCN⁻ structures:

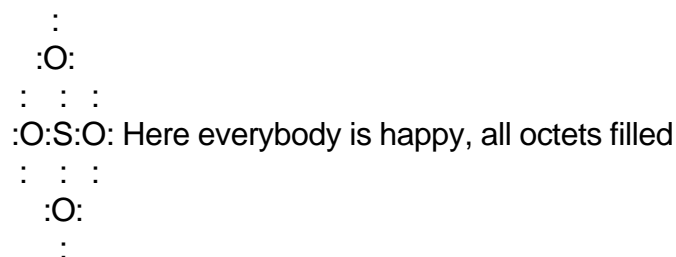
	::S-C≡N:	↔::S=C=N::	↔ :S≡C-N::	
	1	2	3	
e ⁻ in element		S 6	C 4	N 5
e ⁻ in structure	1	7	4	5
F.C.		-1	0	0
F.C.	2	6 0	4 0	6 -1
F.C.	3	5 +1	4 0	7 -2

#3 is the worst because it has 2 atoms with non-zero formal charge

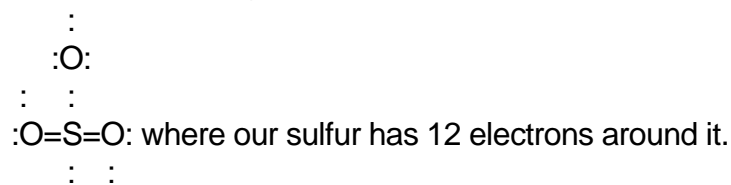
Since the electronegativities are: S 2.5, C 2.5, and N 3.0, structure 2 is better than 1 because it has the negative formal charge on the most electronegative N

Another example, SO₄²⁻

One Lewis structure we can come up with for this is:



If we assume however that since sulfur is in the third row, it might be happy with more than an octet, we can get several other structures, one of which is:



Which structure is better? Let's assign formal charge to each atom
 In the first structure each oxygen has 6 lone pairs electrons and 1 shared Pair of electrons for a total of 7 valence electrons In an uncharged state it would have 6 valence electrons to it has a net FORMAL charge of -1

For the Sulfur we have 8 shared pairs for 4 valence electrons when it was 6 in the elemental state to this is +2 so our formal charges are +2, -1, -1, -1, -1 (total of -2 for consistency check)

In the second model we have 1 oxygen at -1, 2 oxygens at $6-6 = 0$ and the sulfur at $6-6 = 0$ for a net of 0, -1, -1, 0, 0. So this model has more charges close to zero and is therefore considered the better model. Can actually make several resonance forms of this as well.

Odd-electron molecules

A very few compounds exist that contain an odd number of molecules. Perhaps the most common example is NO (From O_2 and N_2) in auto exhaust. Since our model depends on using electron pairs, it will not accommodate such compounds easily. For now we will ignore these guys.

Summary of formal charge rules

1. Sum all lone pair electrons and $\frac{1}{2}$ of each shared pair of electrons
 2. Subtract the above number from the number of valence electrons expected for the element
- Check Sum of formal charge should equal net charge of ion
 - If nonequivalent Lewis structures exist, one with most formal charges close to zero and negative charges on most electronegative atoms are best.

Note 1. Formal charge is an estimate of charge on an atom, they are not the actual charge

Note 2. Sometimes Lewis structures will give you an incorrect model, always check a model against experimental data.

8.13 Molecular Structure: The VSEPR Model

[Bring in Demo Models](#)

[Handout VSEPR Summary End of chapter](#)

The 3-D structure of a molecule plays an important role in its reactivity. For example the difference between a raw egg white and a cooked egg white isn't that chemical bonds have been made and broken, it's that the 3-D structure has been rearranged. Even the simplest of chemical properties like polarity, depends on an understanding of molecular structure.

To help you to be able to predict the 3D structure of a simple molecule you will use a model called the **valence shell electron pair repulsion model (VSEPR)** a model useful in predicting the structure of molecules forms from nonmetals

The whole idea behind this model is that *the structure around a given atom is determined primarily by minimizing electron pair repulsions*

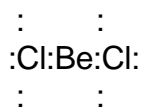
Thus bonding and non-bonding pairs of electrons will be positioned as far as possible from each other.

Let's start by going through the different structures in the handout in order

VSEPR Handout - Last page of notes

1. BeCl_2

Lewis structure:



There are only 2 pairs of electrons around the Be atom. So there are **2 electron regions**. How can we get them as far apart as possible from each other? Place at 180° apart.

We call this structure linear, and, since there are no lone pairs, the molecular and electronic structure are both the same, linear.

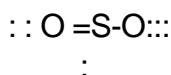
2. BF_3



$\text{:} \text{:} \text{:}$ Note here is the example of an electron deficient B we had earlier
 :F:B:F: There are three electron regions, and the way to get these 3 bonds away from each other is to put them at 120° apart.

We call this structure **Trigonal pyramid**. Again there are no lone pairs so the molecular and electronic structures are the same.

3. SO_2



Looking at the S, the double bond counts as one electron region, the double bond as another electron region, and the lone pair as a third electron region, for a total of 3 electron regions. Again our electronic structure is a trigonal pyramid.

However, what is the molecular structure? In the molecular structure we **ignore the lone pairs** (We can only see atoms, not electrons) That makes this **molecular structure V-shaped**.

4. CH₄

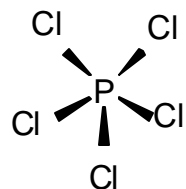
H 4 single bonds, 4 electron regions.
 | If the molecule was planar like this piece of paper, you get four 90's.
 H-C-H However, the structure is 3 dimensional and has 109.5° and get further spread.
 | We call this structure a **Tetrahedral**
 H So *whenever 4 pairs of electrons around an atom, should be Tetrahedral*

5. NH₃

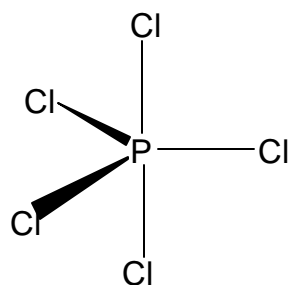
H
 | the lone pair counts as an electron region, so 4 electron regions
 H-N: This makes our electronic structure tetrahedral, but what about the
 | Molecular structure? This is a trigonal pyramid
 H Technically the lone pair 'pushes' a little harder than the electrons in
 A bonding pair, so this distorts the tetrahedral a bit. This makes the angles
 actually <109.5° but I'm not very picky about this fine point.

6. H₂O

: 4 electron regions, electronic structure = tetrahedral
 H-O-H Ignoring the lone pairs, the molecular structure is V-shaped
 : Again the bond angles are actually somewhat less than 109.5

7. PCl₅

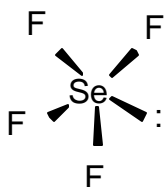
5 electron regions. How do we get these away from each other?
 One straight up, one straight down, 3 even about the equator



We call this structure a **trigonal bipyramid**

There are 90 angles between the up and down Cl's and the one at the equator, and there are 120 angles between the atoms at the equator.

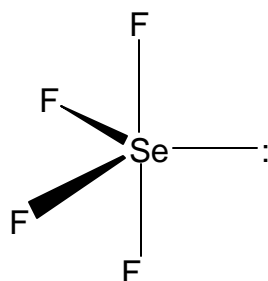
No lone pairs, so molecular and electron structures are identical.

8. SeF_4 

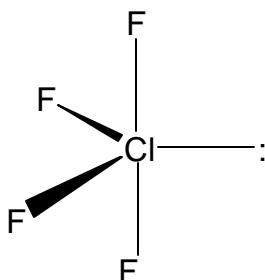
One lone pair, so 5 electron regions, again a trigonal bipyramid electron structure. But what about the molecular structure? We have two nonequivalent places to put the lone pair. Top/bottom or around the equator. If we put the lone pair at the top or bottom, then it has 3 F's located at 90° . If we put the lone pair on the equator, then we have only

2 F's at 90° , and 2 at 120° . This is slightly better.

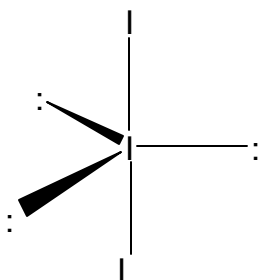
So as a rule **you always put the lone pairs around the equator in a trigonal bipyramid.**



We call this molecular structure a See-Saw (You need to see a demo to see this!)

9. ClF_3 

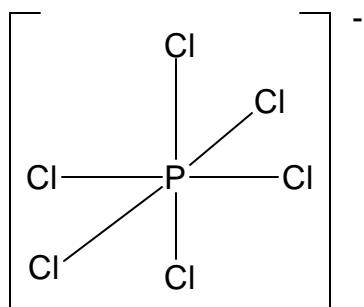
Again 5 electron regions for a trigonal bipyramid electronic structure, but with 2 lone pairs around the equator, the molecular structure is called T-shaped

10. I_3^- 

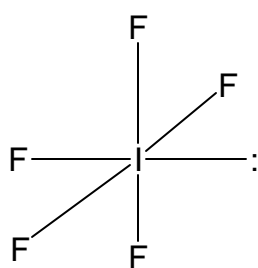
Note: the entire structure has a - charge.

5 electron regions, trigonal bipyramid electronic structure, but a linear molecular structure!

11



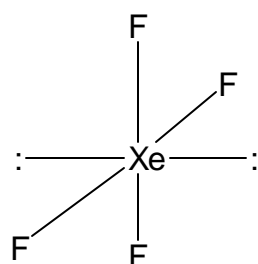
6 electron regions
octahedral electron and molecular geometry

12 IF_5 

6 electron regions
octahedral electron geometry
the lone pair can go any place, there is no difference
the molecular geometry is called square pyramid (Put the lone pair on the bottom to it looks flat, what you have left is a pyramid)

13. XeF_4

6 electron regions



Octahedral electron geometry
The lone pairs go on opposite sides so they don't have to contact each other. The resulting molecular structure is called square planar

Summarizing procedure

1. Draw Lewis structure
2. Count electron pairs and arrange to minimize repulsion
3. Position atoms the way the electrons are arranged
4. Determine the name of the structure from the arrangement of atoms

Let's try an everyday compound, water.

Note that one we have a 3-D structure we have a handle on other properties like does a molecules have a dipole. Given what we have just found, will water have a dipole?
 I_3^- ? SO_4^{2-} (Yes, No, No)

Molecules containing no single central atom

Frequently you may deal with molecules that do not have a single central atom, but have several centers to work with. In this case just apply the rule you have learned to one atom after another. For instance CH_3COOH , acetic acid.

H :O:
 : || : 4 electron pairs so the first carbon is tetrahedral. 3 electron regions in
 H:C:C:O:H the second so it is trigonal, the oxygen had 4 pairs so electrons are
 : : trigonal, but C-O-H bond will be 104-109°
 H

Final Comment

This is a reasonable model to use. It works in many cases. However, there are occasion when it fails so don't trust it blindly.

General Guidelines for Drawing Lewis Structures

1. Lewis structures are only useful for covalent bonding. Don't use for ionic compounds
2. Count the total number of **valence** electrons all the atoms of the molecules. Do not count core electrons. Also remember to add electrons if the molecules is an anion or subtract electrons if it is a cation.
3. Arrange atoms **symmetrically**, with the **least** electronegative atom in the center and the more electronegative atoms around the outside. F and H should always be on the outside with a single bond. Cl, Br, and I are also usually around the outside with single bonds.
4. C, N, O, and F, obey the octet rule. C, N, and O are frequently involved in double or triple bonds.
5. In radicals (molecules with an odd number of electrons) use pairs of electrons for each bond, then place the unpaired electron on the least electronegative atom or in a multiple bond.
6. If a single arrangement of atoms can have double bond(s) in more than two equivalent locations you have **resonance** forms present.
7. Nonmetals from the third or higher period may have an **expanded octet**, if they are the central atom in a structure. Place extra lone pairs on this atom. In cases of multiple possible structures the one with the lowest formal charge is best.
8. Be, B, and Al may form compounds with **incomplete** octets. In this case they need to be the central atom.
9. Begin to recognize groups of atoms that are frequently bonded together in different structures. Use these as building blocks to speed up you solution to any complicated structure
10. When finished check your final structure by double checking the total number of valence electrons

Summary of VSEPR Orbital and Molecular Geometries

<u># electron regions</u>	<u># non-bonding pairs</u>	<u>Orbital Geometry</u>	<u>Bond angles</u>	<u>Molecular geometry</u>	<u>Example</u>
2	0	linear	180	linear	BeCl ₂
3	0	trigonal-planar	120	Trigonal planar	BF ₃
	1	trigonal-planar	120	V-shaped	SO ₂
4	0	tetrahedral	109	Tetrahedral	CH ₄
	1	tetrahedral	<109	Trigonal pyramid	NH ₃
	2	tetrahedral	<109	V-shaped	H ₂ O
5	0	trigonal bipyramid	120&90	Trigonal bipyramid	PCl ₅
	1	trigonal bipyramid	<120&90	See-saw	SeF ₄
	2	trigonal bipyramid	<120&90	T-shaped	ClF ₃
	3	trigonal bipyramid	180	Linear	I ₃ ⁻
6	0	octahedral	90	octahedral	PCl ₆ ⁻
	1	octahedral	<90	Square pyramid	IF ₅
	2	octahedral	<90	Square planar	XeF ₄