

CH. 1 - Introduction Structure and Bonding

What is Organic chemistry: Organic chemistry is the study of compounds that contain carbon. All organic compounds contain carbon.

Originally it was thought that organic compounds were somehow living material or produced only by living systems. We now know that this is not true. A chemist working in the laboratory can make organic compounds that are exactly the same as the organic compounds found in nature.

All the compounds in living systems contain carbon and are therefore organic compounds. Examples of some important biological molecules are:

- Proteins
- DNA
- All tissues in the body
- All plant material such as wood

Many synthetic organic compounds are very useful. Some examples are:

- Drugs – Virtually all modern drugs are organic compounds.

- Plastics

- Nylon, polyester

- Synthetic rubber

- Fuels, such as gasoline and cooking gas, and also things like motor oil and antifreeze

- Paper products

- Paints

- Dyes

- Soaps

- Perfumes, cosmetics

In some ways organic chemistry is easier than general chemistry because we will focus on only a few of the elements, mainly those in the first and second rows of the periodic table. The main elements we need to know are:

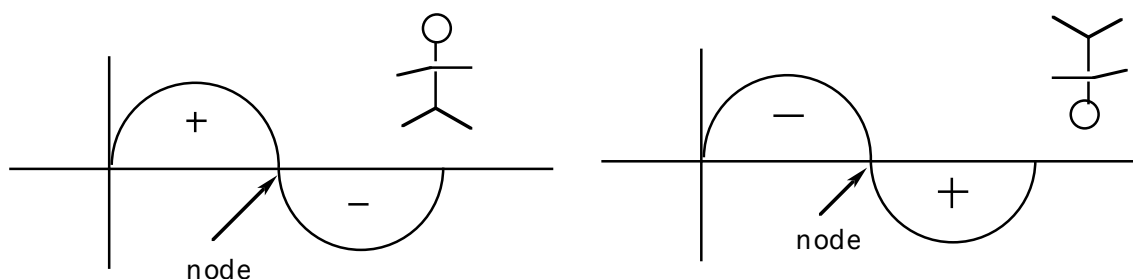
Carbon (C), Hydrogen (H), Boron (B), Nitrogen (N), Oxygen (O), and the halogens (F, Cl, Br, I) and a few others

Electronic Structure of Atoms

Atoms are made up of electrons and protons. The protons are in the nucleus and the electrons travel around the nucleus in defined trajectories called atomic orbitals.

Electrons are very, very small and do not behave like normal particles. In fact, electrons have the properties of both particles and waves. This is the so-called wave-particle duality and it is very hard to understand. Electrons do not move in straight lines like a baseball or a car but move like waves (Fig. 1). In a wave there is the rising part and there is the descending part of the wave. In reality, the signs are arbitrary.

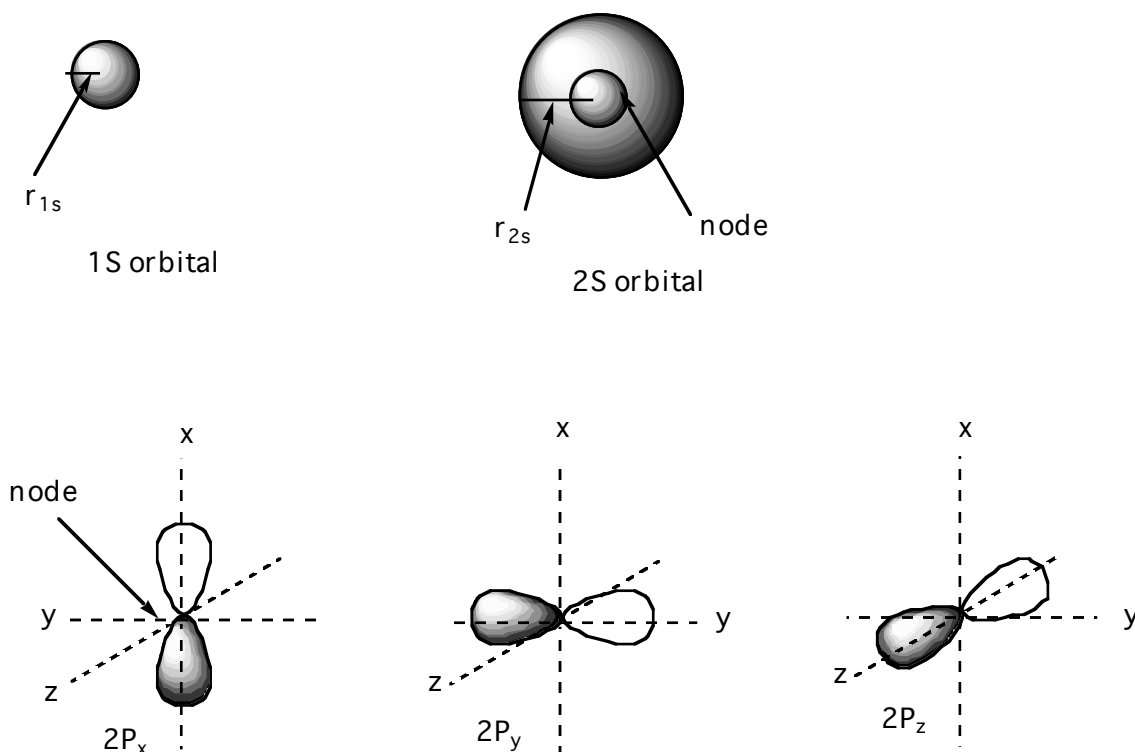
Figure 1.1



Another very strange thing about electrons is that they are very hard to localize precisely. It is impossible to tell where an electron is at any given point in time. Sort of like a wave, it can have an up and down part at the same so that it is spread out over space and fills a certain area of space. We speak in terms of clouds of electron density. This area is what we call an orbital and is described by mathematical equations called wave function. The orbitals represent the probability of finding the electron in a given region of space.

The details of this are not important but what is important is the shape of the simple low-energy orbitals. Fig. 1.2

Figure 1.2 Important Atomic Orbitals



Note that the $1s$ and $2s$ orbitals are both spherically symmetric around the nucleus but the $2s$ orbital is larger ($r_{2s} > r_{1s}$) and that therefore the electrons in a $2s$ orbital are generally farther from the nucleus in the $2s$ than in the $1s$. The nucleus, of course, contains the protons, which have the positive charge. Therefore the electrons in the $2s$ orbital are less tightly held than in the $1s$ orbital and therefore they are higher in energy.

Note also that the $2s$ orbital has a node.

There are three $2p$ orbitals. Each has the same shape but they have different orientations in space and they each have one node.

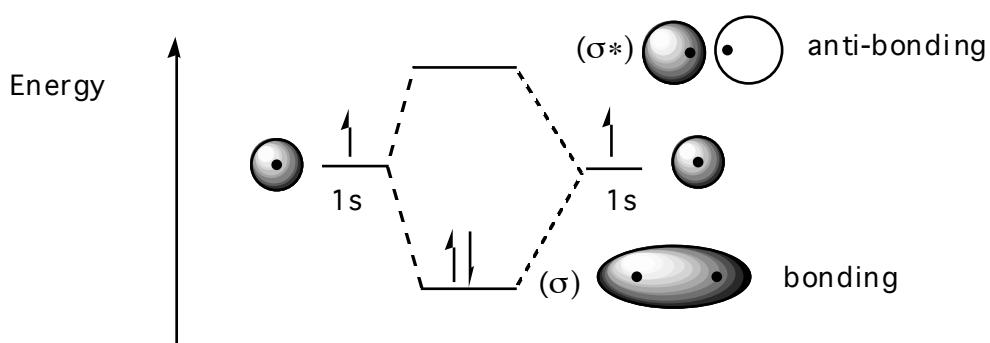
Hydrogen has one proton and one electron. It therefore needs one electron to fill the $1s$ orbital and to become like an inert gas. Therefore, it forms one bond.

Look at its electronic structure.

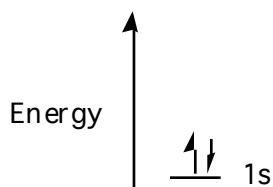
Remember the Rules for Filling Orbitals:

- (1) Fill up the lowest energy orbital first
- (2) Only two electrons can go in any one orbital

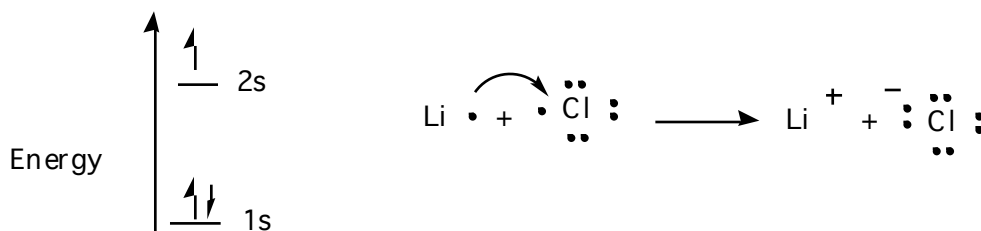
Figure 1.4



Helium has 2 electrons. It has a filled 1s orbital and does not need any more electrons. It is unreactive.



Lithium has three electrons and one valence electron. It will easily donate an electron so that it will then have the filled 1s shell.



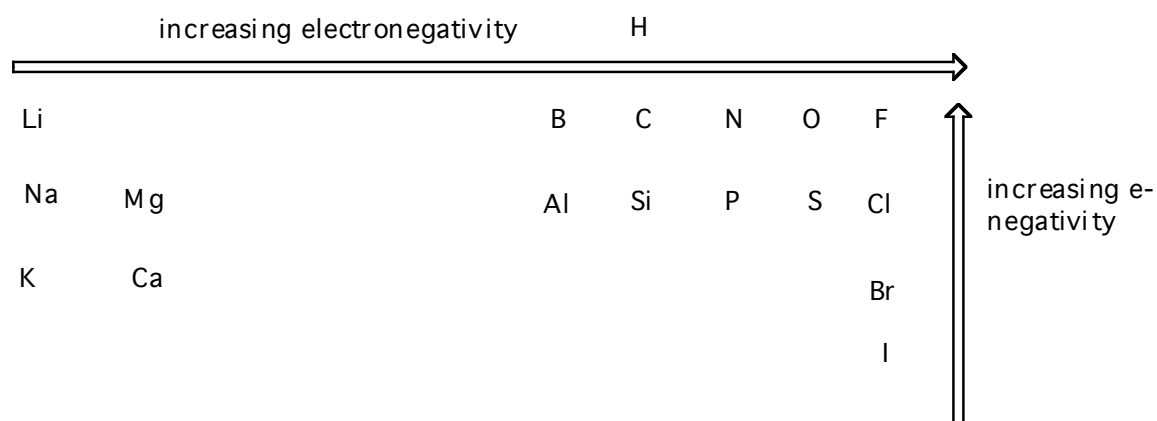
Lithium does not form covalent bonds but forms an ionic bond.

In a covalent bond the electrons are shared more or less equally between the two bonded atoms depending on electronegativity.

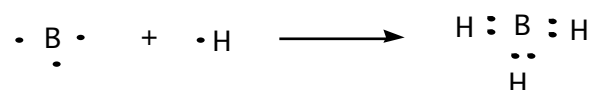
In an ionic bond an electron is transferred from the electropositive element to the electronegative element.

Remember, electronegativity **INCREASES** from **LEFT** to **RIGHT** and **DECREASES** as you go **DOWN** the periodic table.

Figure 1.5

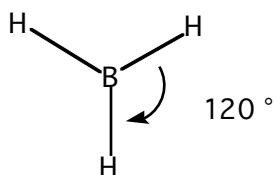


Boron has five electrons, two 1s electrons that are too low in energy to participate in bonding and three valence electrons. Boron forms 3 bonds.



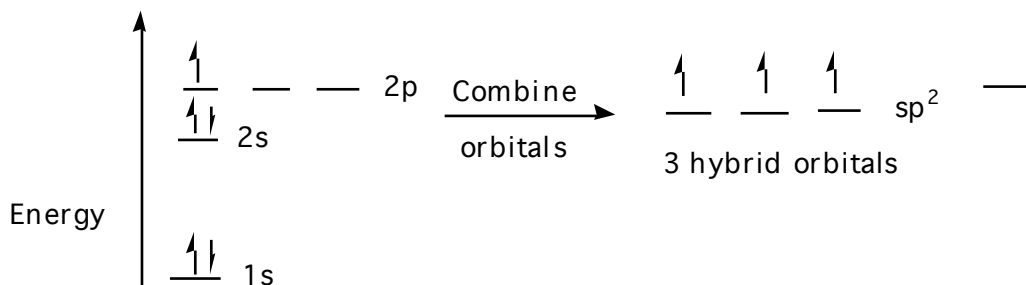
BH₃ itself does not really exist since it is so very reactive. It reacts with itself to form a larger molecule. But if we were to examine the structure of a hypothetical BH₃ in the laboratory, we would find that all three B-H bonds are the same.

And furthermore, we find that the geometry of boron is trigonal planar. The H-B-H bonds are all 120 and the molecule is flat.

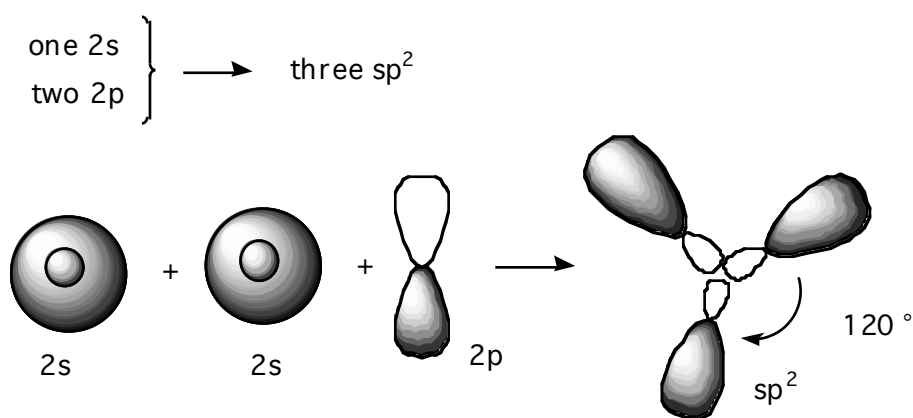


Now we ask, what is the nature of the orbitals that make up these three equal bonds with the angles of 120°.

Look at the electronic configuration of boron.

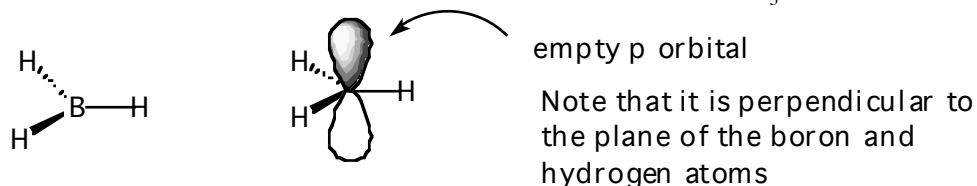


We see that there are two electrons in the 2s orbital and one in the 2p orbital. Since we need three identical orbitals we must combine one 2s orbital and two 2p orbitals to make three sp^2 orbitals.



We get three sp^2 orbitals that are oriented in a trigonal, planar fashion. They are all the same size and shape but have different orientations in space.

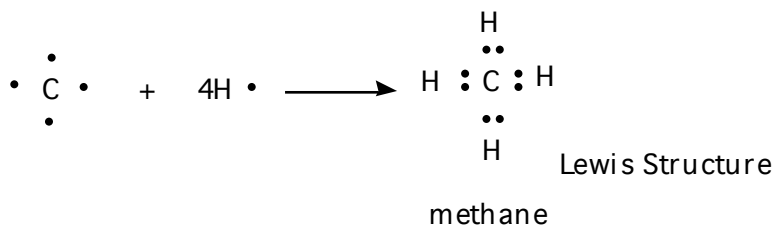
We use these orbitals to form the three identical bonds in BH_3 .



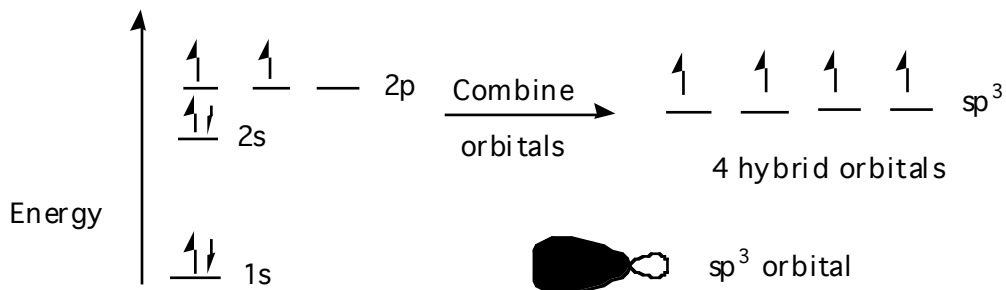
Note that the dashed wedge indicates a bond going into the paper and a solid wedge indicates a bond coming out of the paper

Notice that boron has only six electrons around it. We will see that BH_3 and BX_3 will react so as to GAIN two electrons.

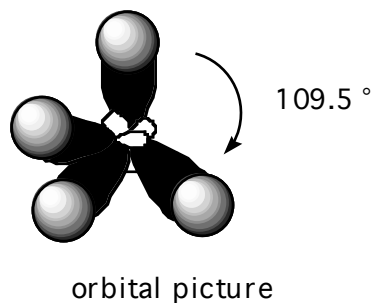
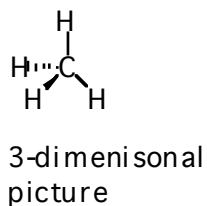
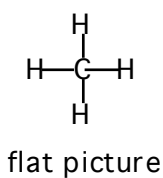
Carbon: has six electrons, four valence electrons and therefore forms 4 bonds.



Again, like with boron, we have the three 2p and one 2s orbital available. In order to make four identical orbitals

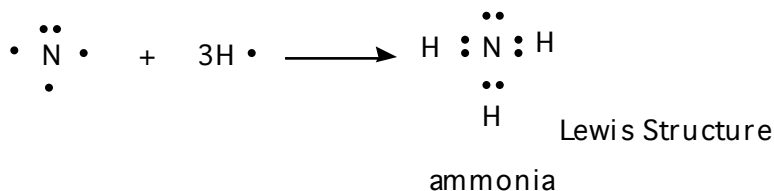
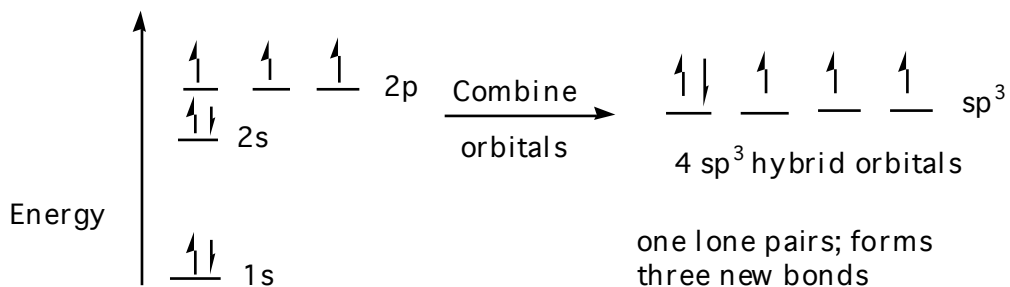


The four new orbitals we make are called sp^3 orbitals. They are similar in shape to the sp^2 orbitals but slightly larger and slightly higher in energy and they are oriented in a tetrahedral fashion.

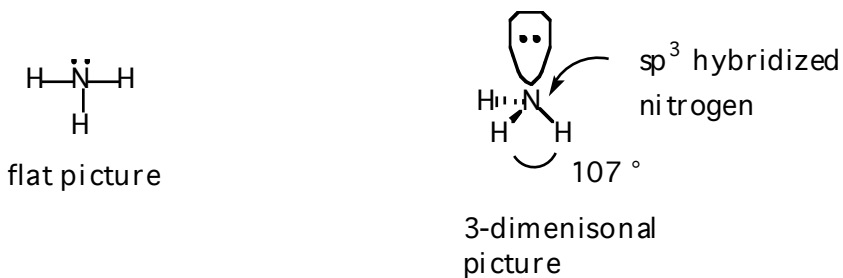


Nature chooses the tetrahedral shape because it is the geometry that will maximize the separation between four objects arranged around a central object. The hydrogen atoms want to be as far apart as possible due to electron-electron repulsion.

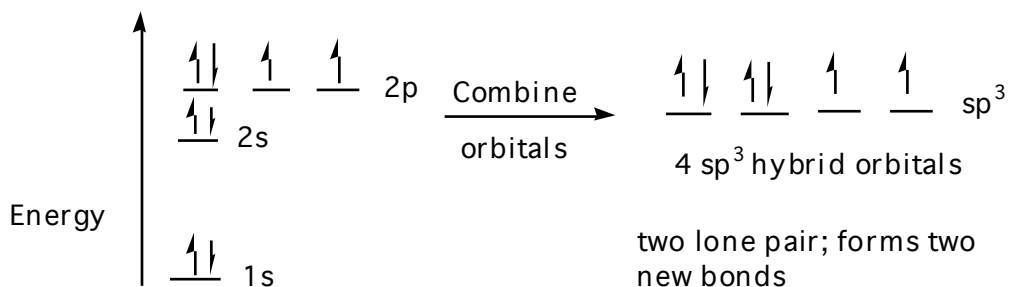
Nitrogen: has seven electrons, 5 valence electrons. Nitrogen forms 3 bonds and has one lone pair.

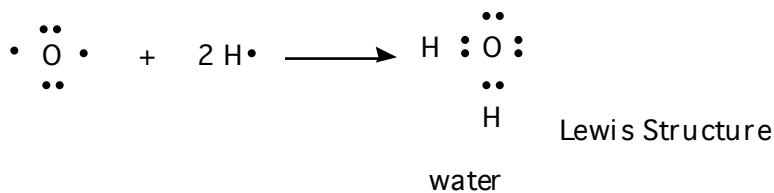


Note that nitrogen has a lone pair of electrons that is available for sharing. If we count the lone pair as one substituent, then ammonia has a tetrahedral shape similar to methane, except that the angles of the H-N-H bonds are slightly smaller than 109.5 since the lone pair substituent is larger than a hydrogen atom

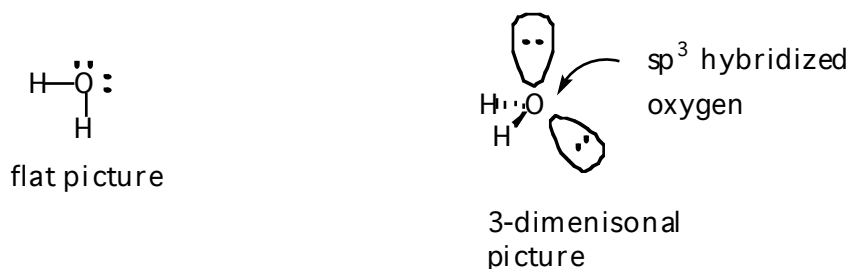


Oxygen: Oxygen has eight electrons, 6 valence electron and forms 2 bonds with two sets of lone pair.





As we know, water is a bent molecule but it is also useful to think of it as tetrahedral in shape with the two lone pair each occupying one of the corners of the tetrahedron. As in ammonia, the lone pair take up slightly more space than the hydrogens. Therefore the H-O-H bond is compressed to 105° from the normal tetrahedral value of 109.5°

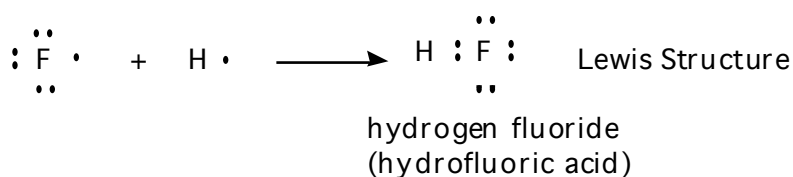
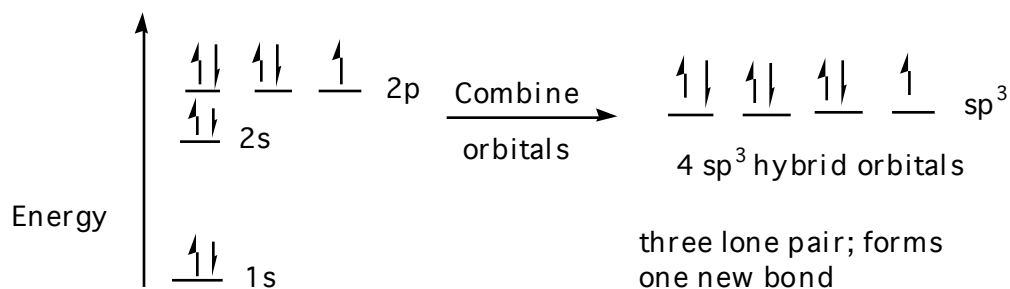


Halogens: These each have 9 electrons, 7 valence electrons and each form 1 bond with three sets of lone pair.

The halogens are:

Fluorine, F
Chlorine, Cl
Bromine, Br
Iodine, I

The electronic structure of fluorine is

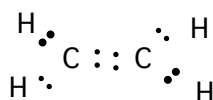


Multiple Bonds Between Atoms

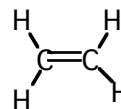
Carbon and other atoms are capable of forming more than one bond by sharing four or even six electrons between two atoms.

For example:

We can have a carbon-carbon double bond as in ethylene.



ethene



Note that each line represents two electrons

Note that four electrons are shared between the two carbon atoms and that we can represent each pair of electrons with a line.

We can have carbon-carbon triple bonds



linear

ethyne (acetylene)

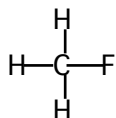
Writing Lewis Structures:

Example: Write the Lewis structure for CH_3F .

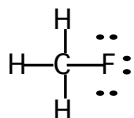
(a) Find the number of valence electrons for all the atoms. This is the same as the group number. If the structure is an ion, add an electron for a (-) charge and subtract an electron for a (+) charge.

$$\begin{array}{ccccccc} 4 & + & 3(1) & + & 7 & = & 14 \\ \uparrow & & \uparrow & & \uparrow & & \\ \text{carbon} & & \text{hydrogen} & & \text{fluorine} & & \end{array}$$

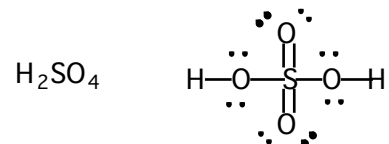
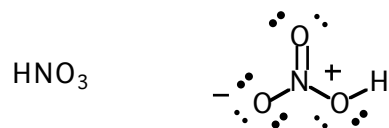
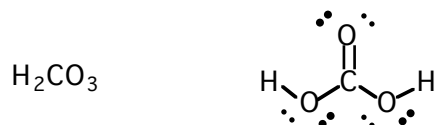
(b) Use pairs of electrons to form bonds between all atoms that are bonded to each other. Usually we use lines to show the bonding electrons.



(c) Add in the rest of the electrons as lone pair so as to give every atom an octet except for hydrogen, which has only two electrons.



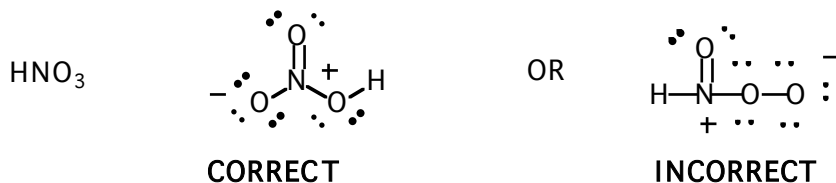
Other Lewis Structures:



Notice that some atoms such as sulfur and phosphorous can have more than four bonds and therefore more than eight electrons.

Note that it is sometimes the case that MORE THAN ONE CORRECT LEWIS STRUCTURE CAN BE WRITTEN FOR A GIVEN FORMULA.

For example:



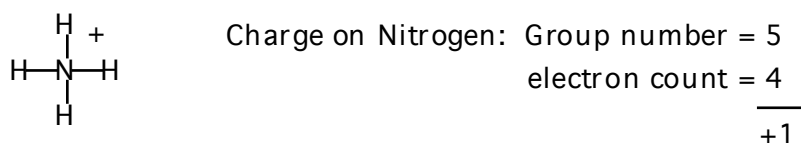
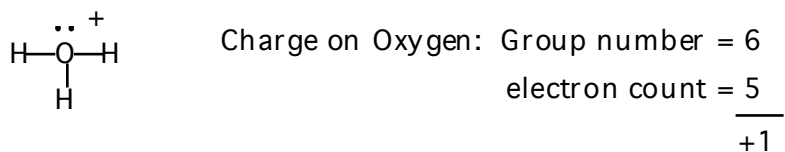
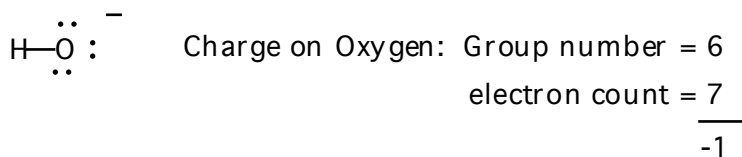
We know from experiments in the laboratory that the correct arrangement of the atoms is the one on the left. Therefore, it is best in this course, when study a new molecule, **LEARN THE CORRECT LEWIS STRUCTURE**. In fact, much of the study of organic chemistry is learning the correct Lewis structure of new molecules.

Another word of caution: Practice drawing the Lewis structures that have been given so far so that you can write them quickly and fluently. On quizzes and exams you will not have time to “work out” the correct arrangement of the atoms but you will NOT be expected to draw correct Lewis structures of molecules you have NOT seen before.

Rules for Assigning Formal Charges:

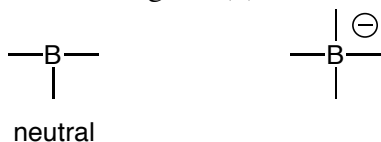
- (1) Assign electron count: count all of the lone pairs and 1/2 of the bonding electrons.
- (2) Subtract this number from the group number.

Examples:

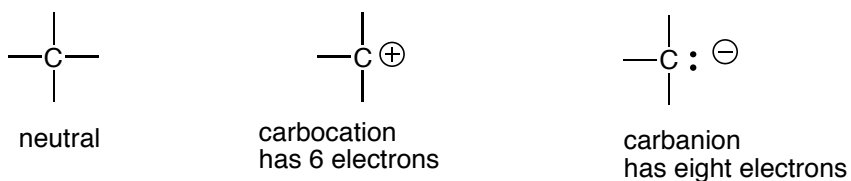


As we can more experience, we should be able to assign the charges automatically. By the second or third chapter you should have practiced this so much that you simply know the charges on all the atoms. Here is a convenient summary.

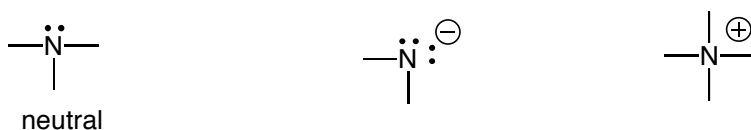
Boron: forms 3 bonds and has 6 electrons around it. With four bonds the boron will now have eight electrons around it but since it shares these two new electrons, it will have a charge of (-)1.



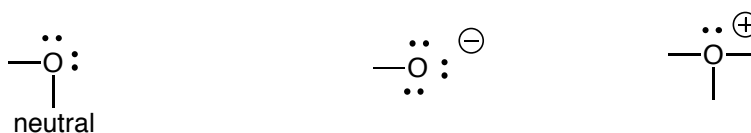
Carbon: Carbon NEVER has five bonds. Usually it forms four bonds. But sometimes it will form very short-lived, reactive intermediates with only three bonds. It can have a (+) or (-) charge depending on the number of electrons.



Nitrogen: Usually forms three bonds. Nitrogen with two bonds has (-) charge; nitrogen with four bonds has (+) charge.



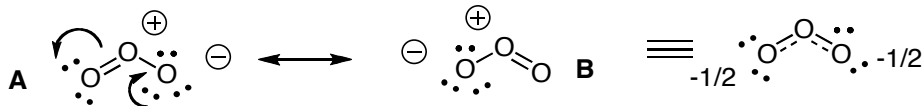
Oxygen: Forms two bonds. Oxygen with one bond has a (-) charge; oxygen with three bonds has a (+) charge.



Resonance Structures

Sometimes more than one correct Lewis structure can be written for a molecule. This is often the case if the molecule contains a double or triple or an empty valence (like a carbocation (H_3C^+)).

Look at Ozone, O_3 , for example:



It looks as if ozone contains an oxygen-oxygen double bond and a single bond but in reality there is only one bond that is mid-way in length (1.28 \AA) between an $\text{O}=\text{O}$ bond (1.21 \AA) and an $\text{O}-\text{O}$ bond (1.47 \AA)

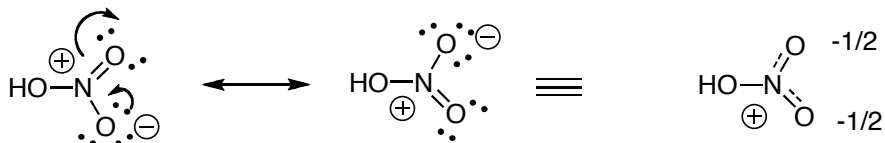
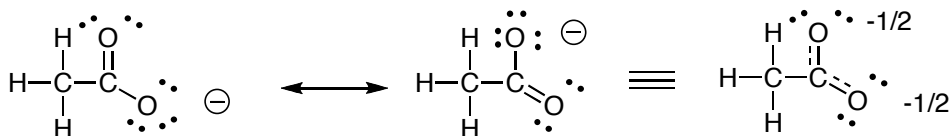
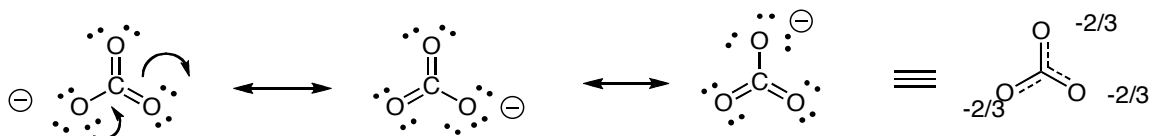
So, we have the concept of resonance. We write two Lewis structures to show that the electrons are spread out over both of the oxygens. This leads to a more stable structure through the dispersal of the charge. Whenever the charge is dispersed

It is important to note that ozone is NOT made up of two different structures that are in equilibrium with each other but there is only ONE structure. The fact that we write two Lewis structures means that one Lewis structure is inadequate for showing the actual charge delocalization and so we need to represent this as two separate drawings (but again there is only one actual molecule).

Another way to show this is to write a Lewis structure with dotted lines as in Structure C above. So, in reality there is a charge of $-1/2$ on each oxygen. The minus charge is equally divided over both oxygens.

Notice too the use of the curved arrows to keep track of the electrons. The **tail** of the arrow shows where the electrons originate from and the **head** of the arrow shows where the electrons go. (More on this below)

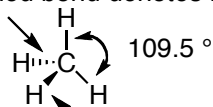
Some more resonance structures:



Shapes of Molecules

CH_4 is tetrahedral. This is the shape that allows the maximum separation between the four hydrogen atoms and – more importantly – the two electrons in each C-H bond.

dashed bond denotes bond going back into paper

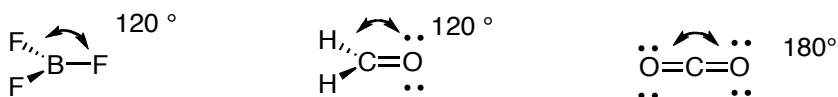


Solid wedge denotes bond coming out of the plane of the paper

H_2O can be considered bent and NH_3 can be described as trigonal pyramidal. It is also useful to think of both of these molecules as tetrahedral with the lone pair occupying vertices:

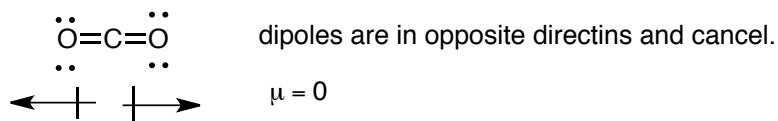


Boron trifluoride, BF_3 , and Formaldehyde, H_2CO , are both trigonal planar, with angles of about 120° . Carbon dioxide, CO_2 , is linear.

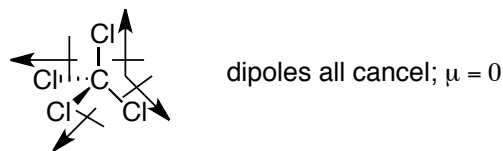


Molecular Dipole Moments

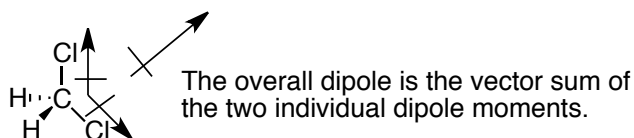
The overall dipole moment of a molecule is a combination of the individual dipole moments and is therefore also a function of the shape of the molecule. For example, CO_2 has two individual dipole moments but the overall dipole moment is zero, since the molecule is linear and the dipoles cancel each other out.



This is also true for carbon tetrachloride, CCl_4 . There are four individual dipoles but they all cancel each other out and the overall dipole moment is 0. Carbon tetrachloride is a non-polar solvent.



But for dichloromethane (also called methylene chloride), CH_2Cl_2 , the dipoles do not cancel and it is a fairly polar molecule.



Curved Arrow formalism

One of the most important keys to understanding organic chemistry is to keep track of the electrons. An excellent way to do this is through use of the curved arrow formalism: the arrow shows where the electron goes and subsequently where bonds are broken and where bonds are formed. For example:



In reaction A, the A-B bond is broken and the species B takes the two electrons in the bond, giving it a lone pair and a minus charge and leaving B with a plus charge. In reaction B, species B, with its lone pair, attacks A to form a new B-A bond.

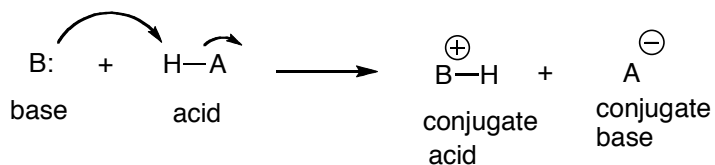
Acid-Base Reactions

There are two major theories of acid-base reactions that we will look at: the Bronsted-Lowry theory and the Lewis theory. They really are the same idea; just that the Lewis theory is a bit more general to include more types of acids and bases.

In the Bronsted theory:

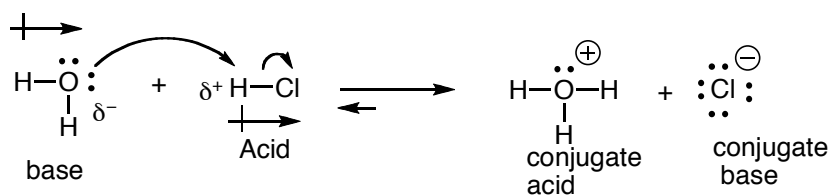
an acid is something that donates protons

a base is something that accepts protons



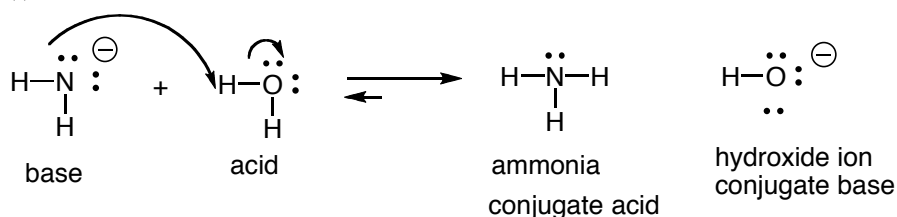
As you can see in this generalized example, the acid gives up a proton to the base. The base must – by definition – have at least a lone pair of electrons or a full minus charge.

Another example:



Note the dipole moments in the reaction above. The oxygen in the water molecule has a partial (-) charge, since it is more electronegative than the hydrogen and the hydrogen in H-Cl has a partial (+) charge since the chlorine is more electronegative. In this reaction, as in many organic reactions, the (-) charge attacks the (+) charge through electrostatic attraction. Again, **pay careful attention to the arrows. They show where the electrons are going.**

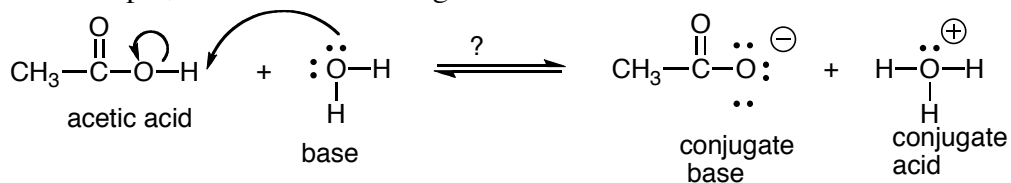
Water can also act as an acid:



Note the position of the equilibrium in each of the acid base reactions shown above. In both of these reactions, the equilibrium lies to the right. How do we predict the position of the equilibrium?

We do this by looking at the pKa's of the acids (and their conjugate bases) involved in the reaction.

For example, look at the following reaction between acetic acid and water:



As we know, the equilibrium constant, K_{eq} is defined as the ration of the products divided by the starting materials:

$$K_{eq} = \frac{\left[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{O}} \right] \left[\text{H}-\overset{\oplus}{\text{O}}-\text{H} \right]}{\left[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H} \right] \left[\text{H}-\overset{\ominus}{\text{O}}-\text{H} \right]}$$

Since this reaction is done with water as the solvent and only a tiny amount of the water is actually converted to H_3O^+ , we can remove the H_2O term from the equation by defining a new term, K_a , where $K_a = K_{\text{eq}}[\text{H}_2\text{O}]$. The equation above then simplifies to:

$$K_a = K_{\text{eq}} [\text{H}_2\text{O}] = \frac{\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}: \\ \cdot\cdot \\ \ominus \end{array} \right] \left[\begin{array}{c} \oplus \\ \cdot\cdot \\ \text{H}-\ddot{\text{O}}-\text{H} \\ | \\ \text{H} \end{array} \right]}{\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{O}-\text{H} \end{array} \right]}$$

We then define $\text{p}K_a$ as equal to $-\log K_a$. The equilibrium constant is a term we can measure by experiment. In the case of acetic acid reacting with water, $K_a = 1.76 \times 10^{-5}$; so $-\log K_a = 4.75$. Notice that in this case, the reaction is unfavorable. The equilibrium lies to the left.

In general:

- the stronger the acid, the weaker the conjugate base. (Note: this is by definition: a strong acid has a weak hold on its proton and therefore the base must have a weak hold on the proton as well)
- the stronger the base, the weaker the conjugate acid

And:

- the smaller the $\text{p}K_a$, the stronger the acid

And:

- a reaction moves in the direction of converting the strong acid into the weaker acid

Or, conversely:

- a reaction moves in the direction of converting the stronger base into the weaker base

Or:

- an Acid-Base reaction is favorable (goes to the right) when the stronger acid is on the left and the weaker acid is on the right

We use the $\text{p}K_a$ tables to give us the strength of the acid. The tables are usually presented with the stronger acids at the top. We can use the $\text{p}K_a$ tables to help us predict the position of the equilibrium in an acid base reaction. (More about this is given below).

To compare which is the stronger acid, ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, or acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, look up the $\text{p}K_a$'s in the table. The smaller the $\text{p}K_a$, the stronger the acid.

Effect of Structure on Acid Strength

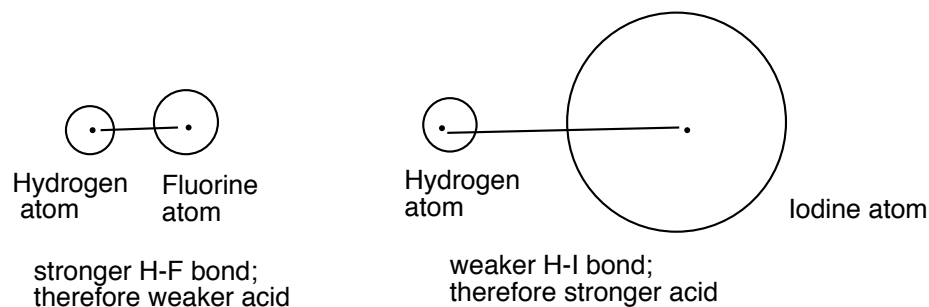
The structure of the molecule greatly affects its acidity. The main factors to consider are:

- (1) The strength of the bond to the atom from which the proton is lost.
- (2) The electronegativity of the resulting anion.
- (3) Resonance stabilization of the anion.

(1) **Bond strength:** In general the weaker the bond to the proton, the more easily it is lost. This can be seen by looking at the halogen acids. The weakest H-X bond is with HI and this is by far the strongest acid. Conversely, HF has the strongest bond and is the weakest acid. Note also that the numbers for the pKa's are exponents, so HI is $10^{13.5}$ times stronger an acid than HF.

	H—F	H—Cl	H—Br	H—I
pKa	3.1	-3.9	-5.8	-10.4
	strongest H-X bond			weakest H-X bond

The H-X bond gets weaker as we go down the column. This is due mainly to the large increase in size of the halogen atom. As the size of the halogen atom gets larger, the hydrogen atom is farther and farther from the nucleus of the halogen and therefore the electron in the hydrogen atom feels less and less of the positive charge in the halogen nucleus. The fluorine atom is only about 30% larger than the hydrogen atom but iodine is much, much larger than hydrogen. This is shown schematically below.



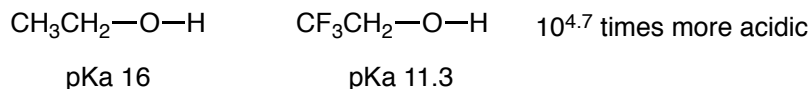
(2) **Electronegativity:** The more electronegative the atom attached to the proton, the stronger the acid. The electronegative atom attracts the two electrons in the H-Y bond, making a stronger dipole moment and weakening the bond.

	small dipole			large dipole
	H ₃ C—H	H ₂ N—H	HO—H	F—H
pKa	60	36	15.7	3.1
electro- negativity	2.55	3.04	3.44	3.98
	least electroneg. atom, least acidic			most electroneg. atom, most acidic

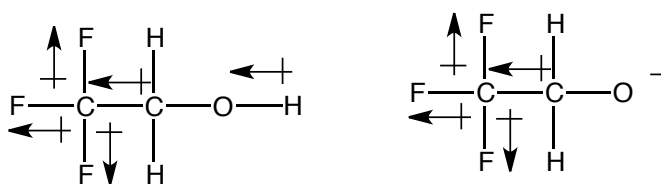
Note that for atoms in the same group (same column), the bond strength is more important than the electronegativity. H-I (pKa -10.4) is a much stronger acid than HF (pKa 3.1) even though fluorine (e^- neg. 3.98) is much more electronegative than iodine (e^- neg. 2.66).

The electronegativity is important when comparing atoms in the same row.

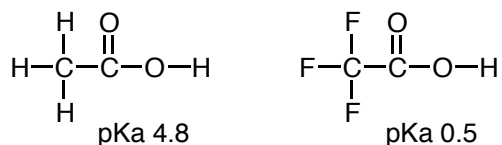
Electronegative substituents near to the acidic proton can increase the acidity.



The electronegative fluorine atoms withdraw electron density from the C-F bonds which polarizes the $\text{CF}_3\text{—CH}_2$ bond which in turn helps to withdraw electron density from the O-H bond, weakening it. The resulting anion is also stabilized by the fluorines since they help to disperse the negative charge of the anion by electron withdrawal.

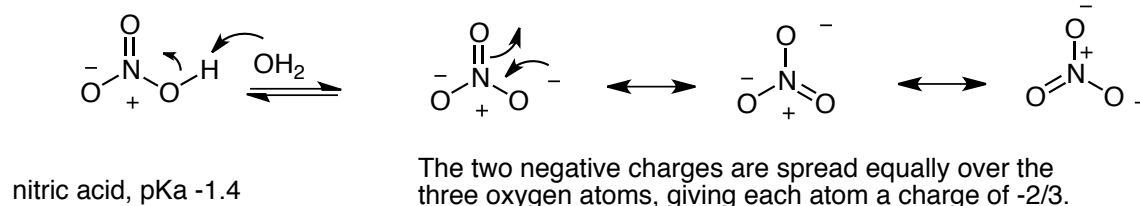
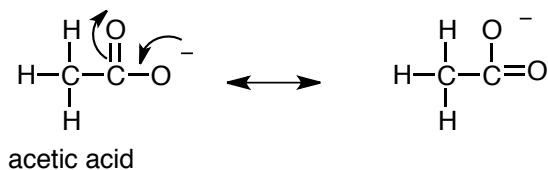


This electron withdrawal by an electronegative atom is called the inductive effect. It is transmitted through the bonds. Another example:



(3) Resonance Stabilization of the Resulting anion:

When the anion is attached to an atom that in turn is attached to an atom that contains a double bond, resonance stabilization of the anion is possible. The negative charge can be delocalized over two or more atoms and this leads to a significant lowering of the energy.



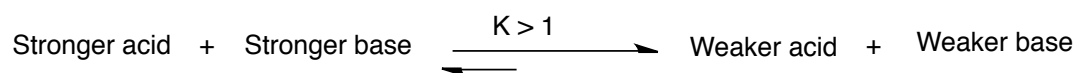
The Position of the Acid-Base Equilibrium

It is critical when designing chemical reactions to be able to predict the position of the acid-base equilibrium. As we have said, the reaction proceeds in the direction that converts the stronger acid to the weaker acid and the stronger base to the weaker base.

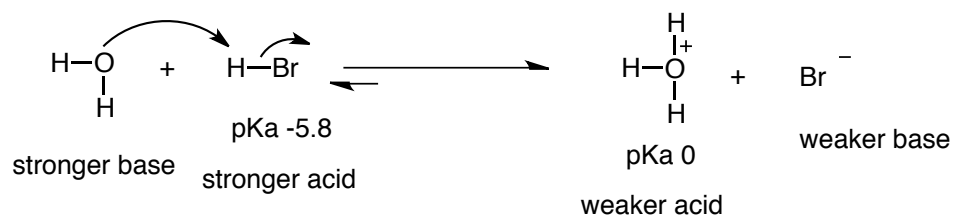
For:



In general:



For example:



We can predict the equilibrium constant by comparing K_a 's:

$$K_{\text{eq}} = \frac{K_a \text{ of reactant acid}}{K_a \text{ of product acid}}$$

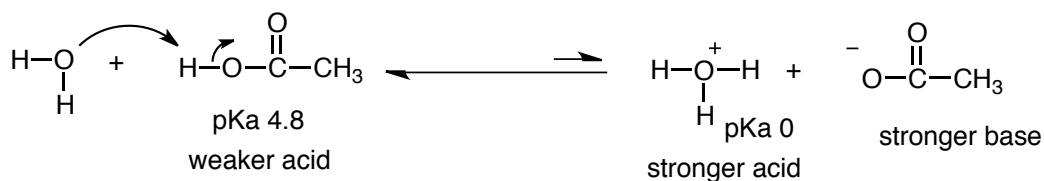
$$\text{Since } 10^{-\text{p}K_a} = K_a$$

Therefore,

$$K_{\text{eq}} = \frac{10^{-\text{pKa of reactant acid}}}{10^{-\text{pKa product acid}}} = \frac{10^{5.8}}{10^0} = 10^{5.8}$$

So, in the case K_{eq} is favorable, lying well to the right.

For:

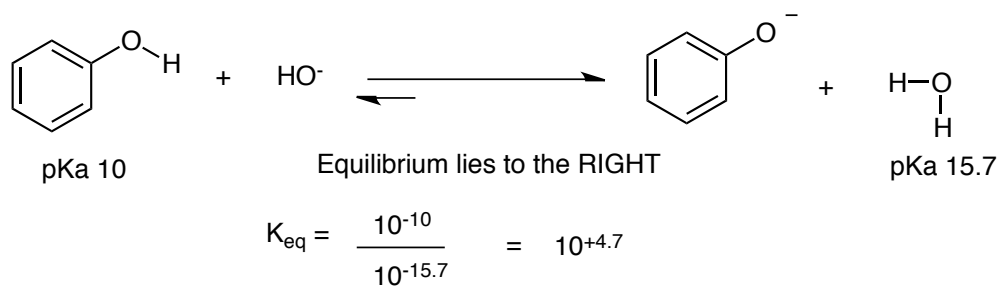


$$K_{\text{eq}} = \frac{10^{-4.7}}{10^0} = 10^{4.7} \quad \text{Equilibrium lies to the LEFT}$$

In general, when we speak of a strong acid, we mean it is stronger than H_3O^+ and a weak acid is weaker than H_3O^+ .

And a strong base is one that is stronger than hydroxide, HO^- , and a weak base is one that is weaker than hydroxide.

So to predict the direction of proton transfer we can use the following useful generalization: Proton transfers from an acid to a base that lies above it in Table 1.8 are unfavorable.



Again, if the pKa of the conjugate acid of the base is larger than the pKa of the acid, the equilibrium lies to the RIGHT. If not, it lies to the LEFT.

Lewis Acids and Lewis Bases

This is a more general definition of an acid and a base. According to the Lewis definition, an acid is any species that accepts an electron lone pair. A Lewis acid needs electrons. Some common Lewis acids are: H^+ , BX_3 , AlX_3 , H_3C^+ (a carbocation). There are others we will encounter as we go through the course.

A Lewis base is any species that can donate an electron pair. So, any species with a lone pair is a Lewis acid. Examples include H_2O , HO^- , H_3N , Cl^- , F^- , Br^- , I^- , etc.

Examples of Lewis acid-base reactions:

