# Chem 1045 Lecture Notes

# Chemistry & Chemical Reactivity Kotz/Treichel/Townsend, 8th Ed

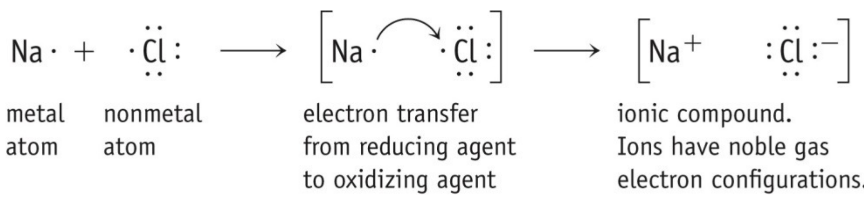
**These Notes are to <u>SUPPLEMENT</u> the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, <u>READ THE CHAPTER</u> prior to the Lecture, bring in these lecture notes and make comments on these notes. These <u>notes alone are NOT enough to pass any test! The author is not responsible for errors in these notes</u>.**

## Chapter 8 Bonding and Molecular Structure <u>29-July-2013 DRAFT</u>

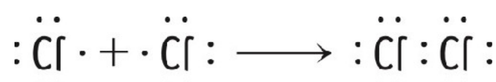
**Structure** is the arrangement of atoms in 3D space
**Bonding** describes the forces that hold adjacent atoms together.

**Chemical Bond** is the net attractive force that occurs between atoms

**Ionic Bond** involves the transfer of one or more valence electrons from one atom to another




**Covalent Bond** shares electrons between atoms:



Other Covalent Bond Examples include the diatomic gases $O_2$ and $N_2$ as well as H2O, $CO_2$, the organic compound Methane – $CH_4$, the polyatomic ions $CO_3^{2-}$, $CN^-$, $NH_4^+$, $NO_3^-$ and $PO_4^{3-}$. Note these consist of nonmetal atoms, metal atoms use Ionic Bonding.

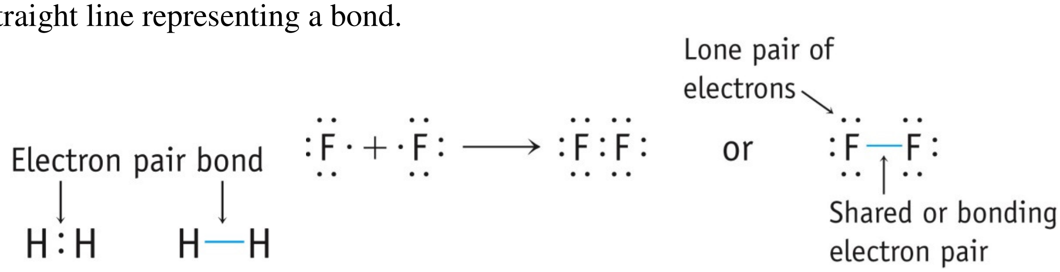
**Valence Electrons** represent the outer shell of electrons that are responsible for chemical reactions and bonding. These usually are the outermost s and p shell.
**Core Electrons** are the inner electrons that are not involved in bonding or chemical reactions.

**Table 8.1 Core and Valence Electrons for Several Common Elements**

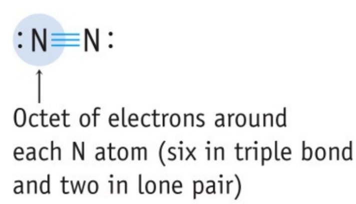
| Element | Periodic Group | Core Electrons | Valence Electrons | Total |
|---|---|---|---|---|
| *Main Group Elements* | | | | |
| Na | 1A | $1s^22s^22p^6$ = [Ne] | $3s^1$ | [Ne]$3s^1$ |
| Si | 4A | $1s^22s^22p^6$ = [Ne] | $3s^23p^2$ | [Ne]$3s^23p^2$ |
| As | 5A | $1s^22s^22p^63s^23p^63d^{10}$ = [Ar]$3d^{10}$ | $4s^24p^3$ | [Ar]$3d^{10}4s^24p^3$ |
| *Transition Elements* | | | | |
| Ti | 4B | $1s^22s^22p^63s^23p^6$ = [Ar] | $3d^24s^2$ | [Ar]$3d^24s^2$ |
| Co | 8B | [Ar] | $3d^74s^2$ | [Ar]$3d^74s^2$ |
| Mo | 6B | [Kr] | $4d^55s^1$ | [Kr]$4d^55s^1$ |

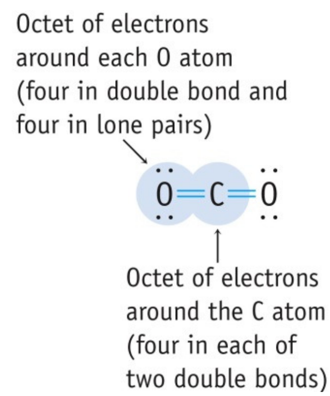
**Lewis Electron Dot Structure and the Octet Rule**

A pair of electrons shared between two atoms represents a bond. Two dots representing the two electrons are changed to a straight line representing a bond.




These two bonding electrons are called a **Bonding Pair**. The six other electron pair on the Fluorine are called **Lone Pair** or **Non Bonding electrons.**




In nitrogen above, remember nitrogen is a diatomic molecule, there are 3 bonding pair and one lone pair on each nitrogen. The molecules try to be in a noble gas configuration – with an $s^2$ and $p^6$ outer shell configuration. It has 8 electrons surrounding it – it has an **Octet of electrons**. The carbon in the carbon dioxide has 4 bonding pair and no lone pair. Each oxygen atom has two bonding pair and two long pair.

Each atom has contributed and accepted electrons to achieve a **Noble Gas Configuration**; they are surrounded by 8 electrons. The **Octet Rule** states the tendency of molecular and polyatomic ions to have structures in which eight electrons surround each atom, $S^2$ $P^6$ = 8 $e^-$.

**Drawing Lewis Electron Dot Structures**

Valence Electrons: Carbon has 4, Hydrogen has 1, Nitrogen has 5 (3 bonding and one lone pair), and Oxygen has 6 2 bonding and 2 lone pair). Draw the orbital box diagram or the spdf notation and prove it to yourself!

**Table 8.2 Lewis Electron Dot Symbols for Main Group Atoms**

| 1A $ns^1$ | 2A $ns^2$ | 3A $ns^2np^1$ | 4A $ns^2np^2$ | 5A $ns^2np^3$ | 6A $ns^2np^4$ | 7A $ns^2np^5$ | 8A $ns^2np^6$ |
|---|---|---|---|---|---|---|---|
| Li· | ·Be· | ·B· | ·C· | ·N· | :O· | :F· | :Ne: |
| Na· | ·Mg· | ·Al· | ·Si· | ·P· | :S· | :Cl· | :Ar: |

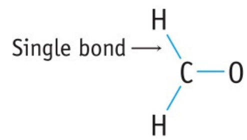
1. Determine the arrangements of the atoms in the molecule, determine the central atom.
2. Determine the total number of electrons in the molecule
    a. For a neutral atom, the # of $e^-$ is the sum of the valence $e^-$
    b. For an anion, add the number of electrons equal to the negative charge
    c. For a cation, subtract the number of electrons equal to the positive charge

The number of valence electron pairs = total # of electrons / 2

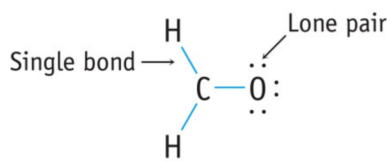
$CH_2O$ Carbon has 4 (from $SP^3$ Hybridization), Hydrogen has 1, Oxygen has 6
= 4 + 2 * 1 + 6 = 12 valence electrons

:C: H :O:

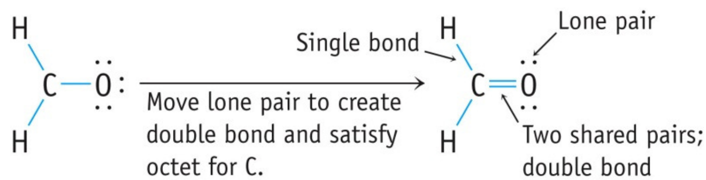
3. Place one pair of electrons between each pair of bonded atoms to form a **single bond**




4. Use any remaining pairs as lone pairs around each terminal atom (except H) so that each terminal atom is surrounded by 8 electrons.




5. If the central atom has fewer than 8 electrons, change one or more of the lone pairs on the terminal atoms into a bonding pair between the central and terminal atom to form a double or triple bond.




**Double bonds** are usually associated with: C=C, C=O, C=N.
**Triple bonds** are usually associated with: C≡C, C≡N, N≡N.
Sulfur and Phosphorous also from double bonds with oxygen S=O and P=O.

**Example 8.1** Draw the Lewis Structures for $CLO_3^-$ and $NO_2^+$

**Example 8.2** Draw the Lewis electron dot structures for $CCl_4$ and $NF_3$.

## Predicting Lewis Structures

The following guidelines help in drawing Lewis Structures. Here are some common bondings:

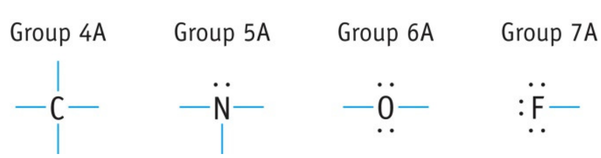
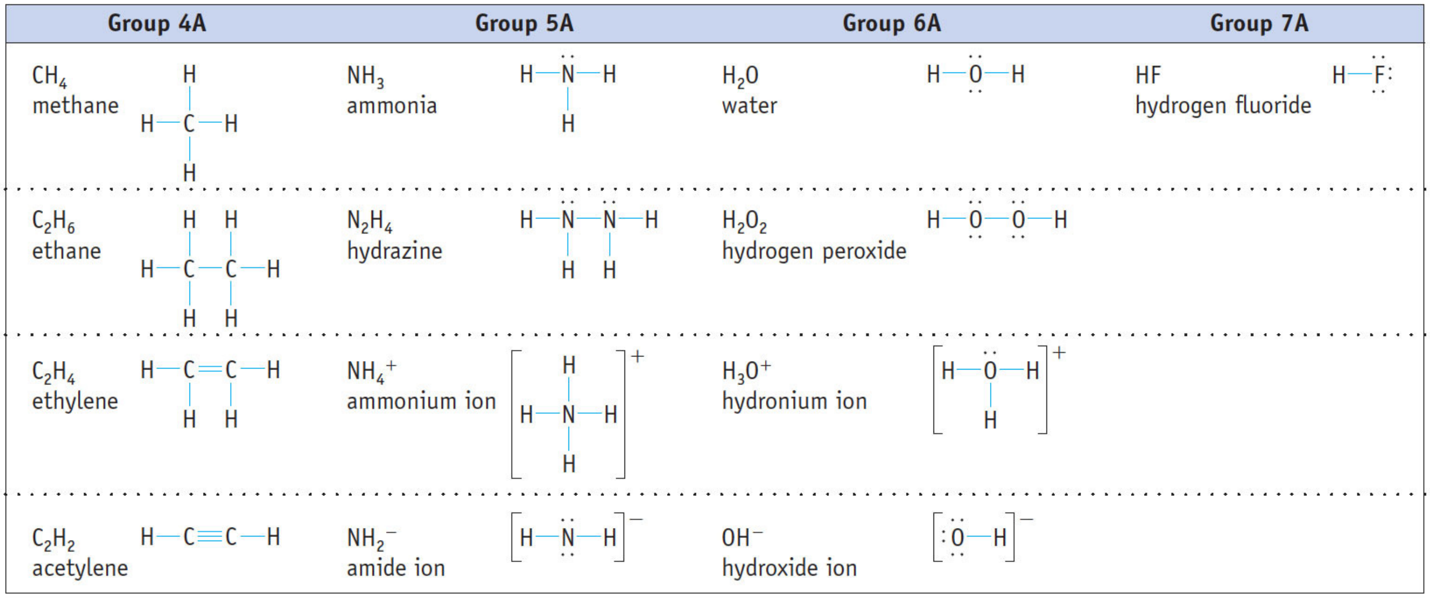
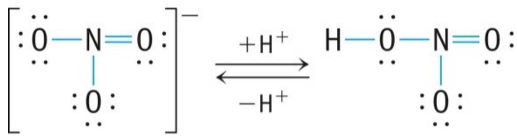


**Table 8.3** Lewis Structures of Common Hydrogen-Containing Molecules and Ions of Second-Period Elements



| Group 4A | Group 5A | Group 6A | Group 7A |
|---|---|---|---|
| $CH_4$ methane | $NH_3$ ammonia | $H_2O$ water | HF hydrogen fluoride |
| $C_2H_6$ ethane | $N_2H_4$ hydrazine | $H_2O_2$ hydrogen peroxide | |
| $C_2H_4$ ethylene | $NH_4^+$ ammonium ion | $H_3O^+$ hydronium ion | |
| $C_2H_2$ acetylene | $NH_2^-$ amide ion | $OH^-$ hydroxide ion | |

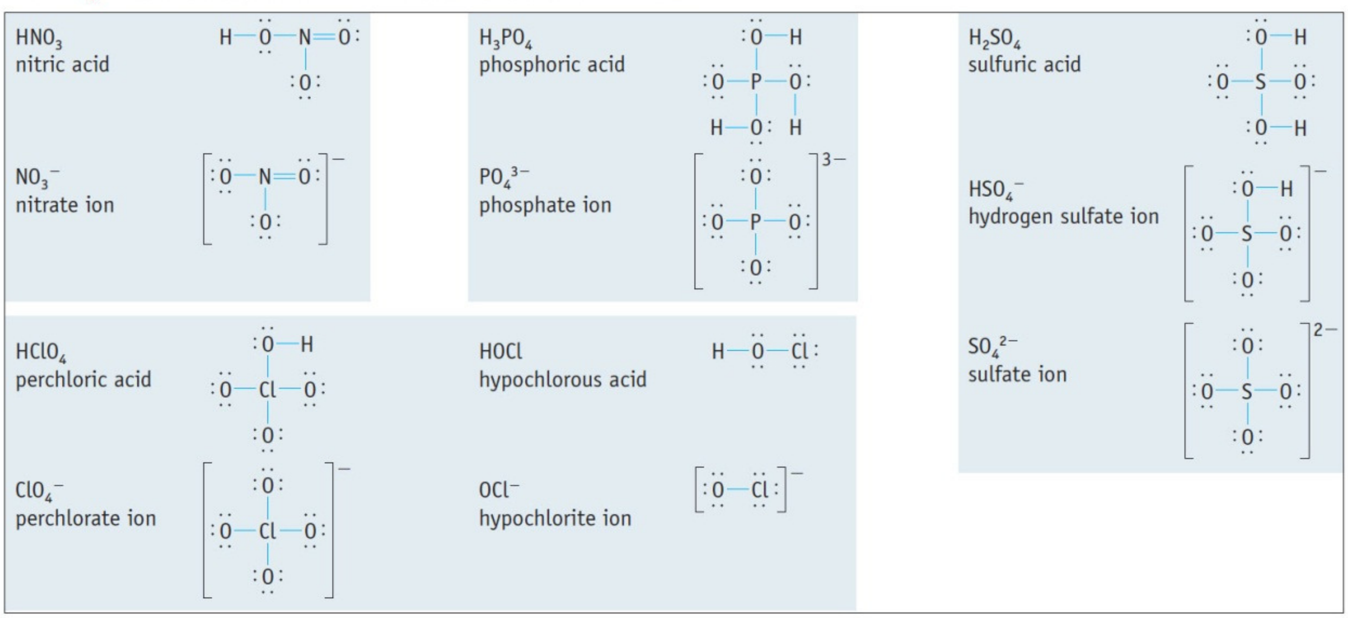
**Oxoacids and their Anions**: in the absence of water, which helps ionize the acid and form hydrogen bonding, these acids form covalent bonds (See Table 8.4 below).




nitrate ion nitric acid

In the above reactions, nitric acid on the right will give up an $H^+$ to water in an aqueous solution to form the nitrate and a hydronium ion. This is what acids do in aqueous solutions. When not in aqueous solutions, most acids are clear, high boiling point liquids.

**Table 8.4** Lewis Structures of Common Oxoacids and Their Anions



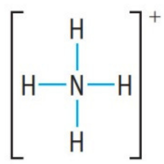
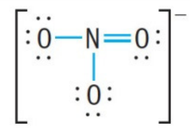
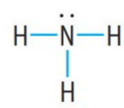
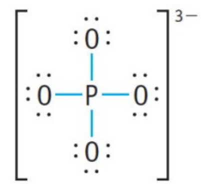
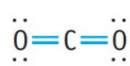
| | | |
|---|---|---|
| $HNO_3$ nitric acid | $H_3PO_4$ phosphoric acid | $H_2SO_4$ sulfuric acid |
| $NO_3^-$ nitrate ion | $PO_4^{3-}$ phosphate ion | $HSO_4^-$ hydrogen sulfate ion |
| $HClO_4$ perchloric acid | HOCl hypochlorous acid | $SO_4^{2-}$ sulfate ion |
| $ClO_4^-$ perchlorate ion | $OCl^-$ hypochlorite ion | |

Isoelectronic species are molecules and ions having the same number of valence electrons and similar Lewis structures. $NO^+$, $N_2$, CO, and $CN^-$ all have 10 valence electrons:

**<u>Work these out</u>**

And here are some more examples to work your mind out:

**Table 8.5 Some Common Isoelectronic Molecules and Ions**

| Formulas | Representative Lewis Structure | Formulas | Representative Lewis Structure |
|---|---|---|---|
| $BH_4^-$, $CH_4$, $NH_4^+$ |  | $CO_3^{2-}$, $NO_3^-$ |  |
| $NH_3$, $H_3O^+$ |  | $PO_4^{3-}$, $SO_4^{2-}$, $ClO_4^-$ |  |
| $CO_2$, $OCN^-$, $SCN^-$, $N_2O$, $NO_2^+$, OCS, $CS_2$ |  | | |

A **Formal Charge** is the charge that resides on an atom or molecule or polyatomc if we assume that all bonding electrons are shared equally:

Formal Charge = Number of Valence e- = [Lone Pair e- + ½ (Bonding e-)]

**Formal Charge = NVE – [LPE + ½ (Be)]**

Take $ClO^-$.    :Cl: + :O:

First arrange the atoms and count the e- (# e- = 7 + 6 = 13)    Cl O

Place a pair of e- between each bonded atom, we have 13 – 2= 11 left    Cl : O

Place remaining e- in pars around each atom    :Cl:O:

But, the compound we have is ClO- not ClO    :Cl:O: -

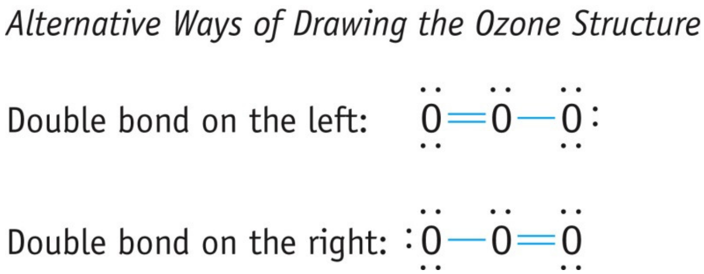
Formal Charge = NVE – [LPE + ½ (Be)] = 6 – [6 + ½ (2)] = -1 For Oxygen
= 7 – [6 + ½ (2)] = 0 For Chlorine

Therefore if a $H^+$ approaches $ClO^-$, it will attach to the oxygen and not the Chlorine!

**Example 8.3** Calculate the formal charge on $ClO_3^-$

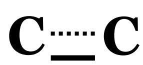
**Oxidation Number and Formal Charge**. **Oxidation numbers** are calculated assuming the bond between an atom pair is Ionic (electrons move to one atom), **Formal Charge** says the electrons in the bond are covalent – they are shared.

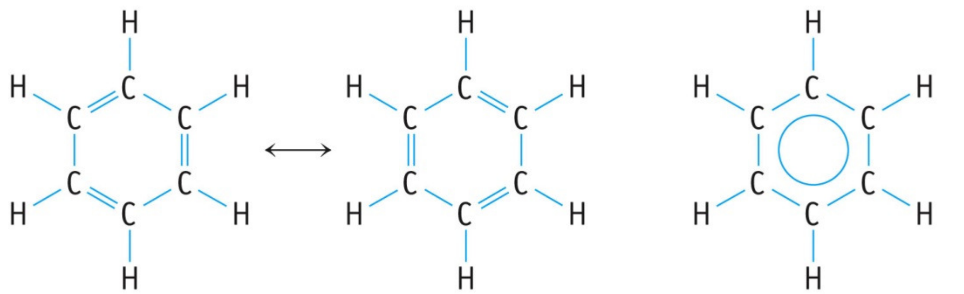
**Resonance structures** are used to represent bonding in a molecule or ion when a single Lewis structure fails to accurately describe the actual electronic structure and/or it's reactive properties.




The double bond on the left structure and the one on the right are called their **Resonance Structures.**
The lengths of both of the end oxygen to center oxygen bonds measure the same length. So, the actual structure is not as presented above but is a **hybrid** or in-between structure.

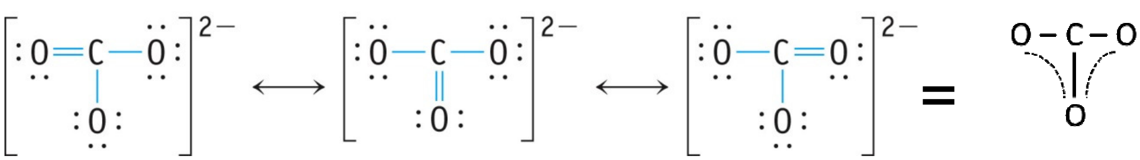
Resonance is used when a single Lewis structure does not describe the actual structure. The actual structure lies somewhere in between two or more presented Lewis structures.

**Benzene,** a common Organic compound also is represented by two resonance structures. The actual structure is an in-between structure as all of the C-C bonds measure the same length. There is not a C-C and a C=C bonds, but there is one bond length 



resonance structures of benzene, $C_6H_6$     abbreviated representation of resonance structures

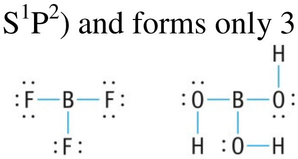
The Carbonate structure for $CO_3^{2-}$ is represented by the following 3 Lewis structures. Actually, all three O to C bonds are the same length and in between the length of a C to O single bond and C to O double bond length.



The Nitrate ion, $NO_3^-$, structure also is represented by 3 Lewis structures similar to the carbonate above.

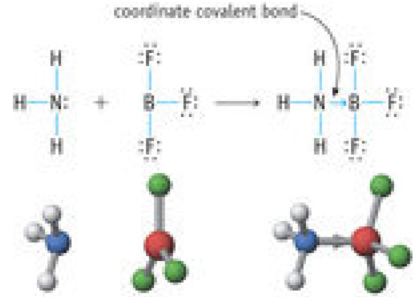
### 8.5 Exceptions to the Octet Rule

Boron has 3 valence electrons (hybridizes to $S^1P^2$) and forms only 3 covalent bonds:



boron trifluoride     boric acid

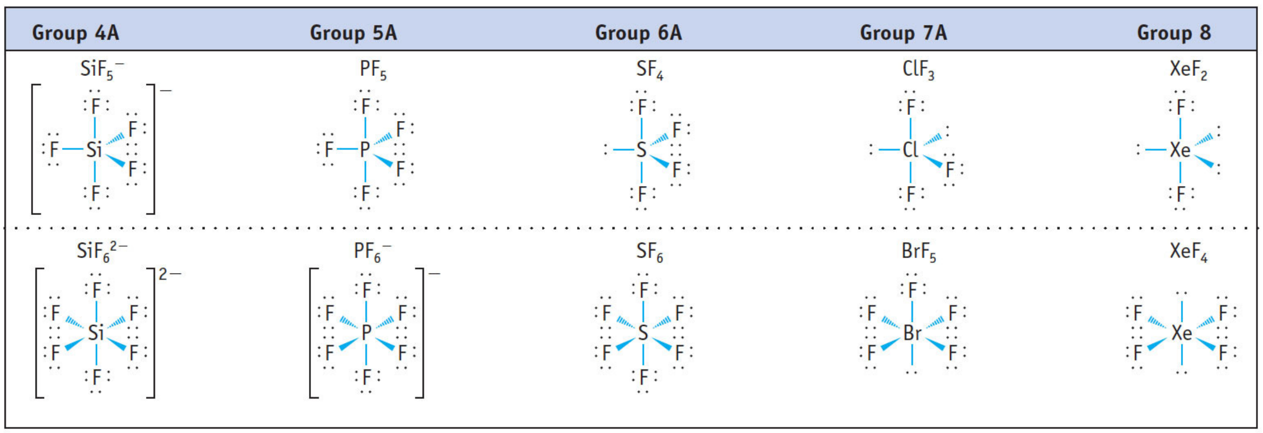
Boron can react with molecules that will donate an electron pair so as to fill the Boron octet. Such bonds are called **Coordinate Covalent Bonds.**




**Compounds with more than 8 valence electrons**

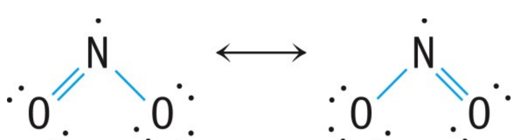
The central atom is surrounded by more than 4 valence electron pairs, most common are F, Cl, and O. Sulfur Hexafluoride, $SF_6$ is also an example. Only elements for n=3 (Periodic Table) or higher form compounds and ions where an octet is exceeded.

Table 8.6 **Lewis Structures in Which the Central Atom Exceeds an Octet**




**Molecules with an Odd Number of Electrons**

**NO** has 11 valence electrons and **$NO_2$** has 17 valance electrons – both an odd number: e.g. There is one unpaired electron!



The unpaired electron is called a **Free Radical**, which usually are very reactive. Free Radicals are responsible for many problems dealing with Mother Nature:

NO from car exhaust reacts with oxygen to form $NO_2$ (toxic to humans at 100 ppm).

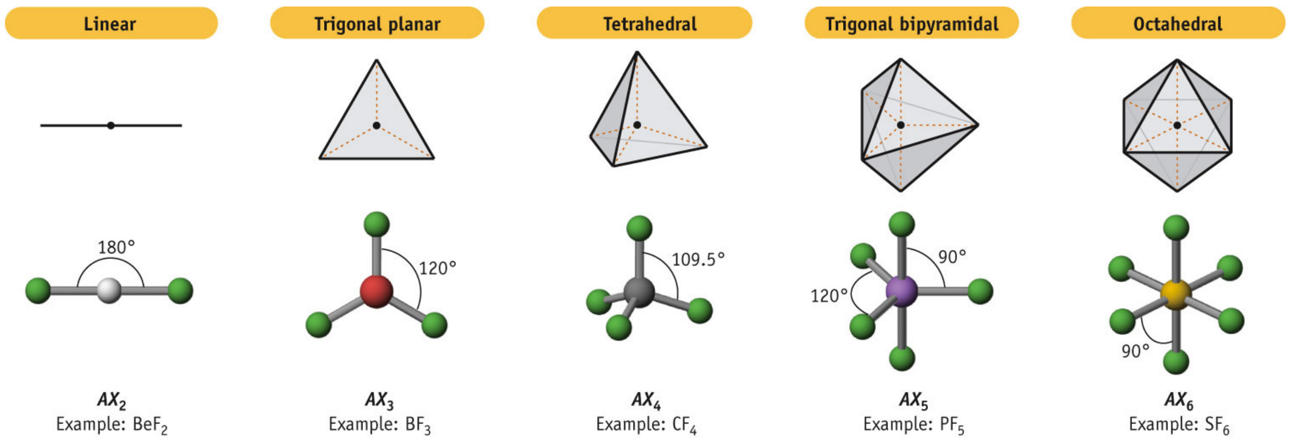
$$NO_{2\,(g)} + H_2O_{(g)} \rightarrow \bullet OH_{(g)} + HONO_{(g)}$$

$$HONO_{(g)} \rightarrow \bullet OH_{(g)} + \bullet NO_{(g)}$$

## 8.6 Molecular Shapes

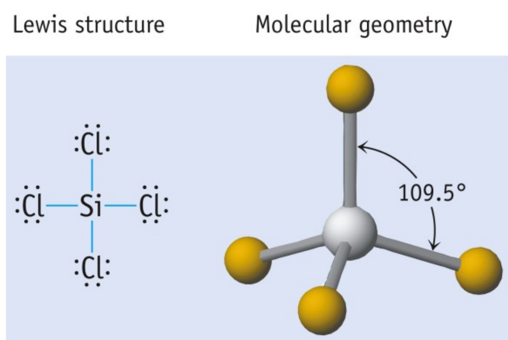
Lewis Structures show a 2D picture of a molecule. For many molecules, a 3D picture is needed in order to understand reactivity. The **Valence Shell electron-Pair Repulsion (VSEPR)** model is used and is based on **the bond and lone pair of electron pairs in the valence shell of an element repel each other and seek to be as far apart as possible.** The positions of the bond and lone pair electrons define the bond angle to the surrounding atoms.

**<u>Single-Bonds</u>** the following geometries vs number of bonds using VSEPR


Two elements tied to a central atom presents a Linear arrangement so the bonding electrons are as far apart as possible. Etc going down the line. Notice the Linear and Trigonal Planar are 2D, the rest are 3D images.

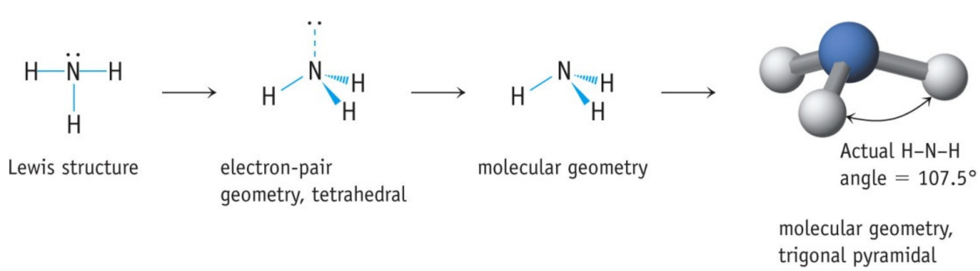
Below is the Lewis Structure (2D) and the Molecular 3D Geometry for $SiCl_4$. This would be the same structure for the organic compound Methane, $CH_4$.




**<u>Single-Bonds with Lone Pairs</u>**

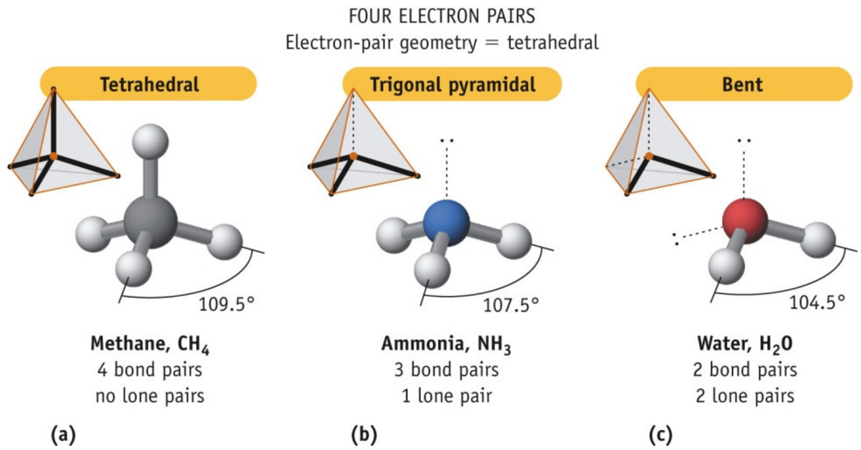
**Electron Pair Geometry:** Geometry assumed by all the valence electron pairs around a central atom. The lone pair of electrons do occupy a special position.

**Molecular Geometry:** Arrangement in space about a central atom



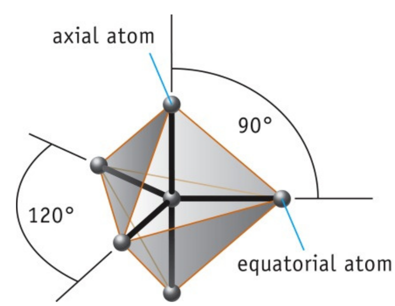
Above is the 2D geometry for Ammonia, $NH_3$. The 3D picture shows the electron pair and how it actually takes up a special position.

**Effect of Lone Pairs on Bond Angles**. Lone Pair of electrons occupy a larger volume than bonding pairs. The angle between the lone pair and a connecting atom will be larger than the angle between two connecting atoms.

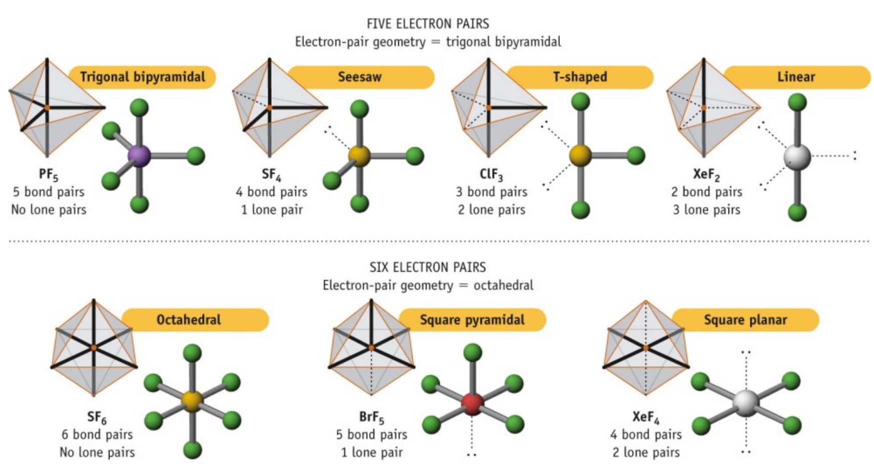



All bond angles in Methane above are equal at 109.5$^o$. The lone pair on Ammonia pushes the three hydrogen's down so the hydrogen-hydrogen angle is no longer 109.5$^o$, but is 107.5$^o$. Water is similar with the two lone pair pushing the two hydrogen back so their angle is 104.5$^o$.

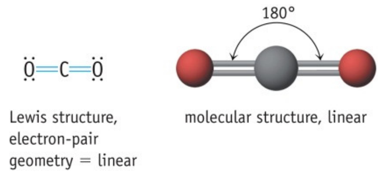
**Central atoms with more than 4 valence electron pair**. When a central atom has 5 or 6 equivalent bonds, all angles are not equal. The trigonal-bipyramidal shown below has two axial locations and three equatorial positions and they are not equivalent. Any lone electron pair would be axial to space them as far away from the equatorial bonds.



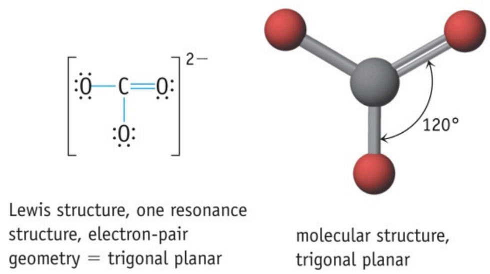

With 6 electron pairs, the shape is octahedral with all angles 90$^o$.



**Multiple Bonds and Molecular Geometry** Double and triple bonds are more complex than single bonds. All of the electrons in a multiple bond occupy the same region of space and therefore count as one bond. Carbon Dioxide has two double bonds, and therefore is linear:




Carbonate ion seems to have one oxygen double bond and two oxygen single bonds. But the bond angles are all the same. So the bonding is a Resonance Hybrid of one double bond and two single bonds:

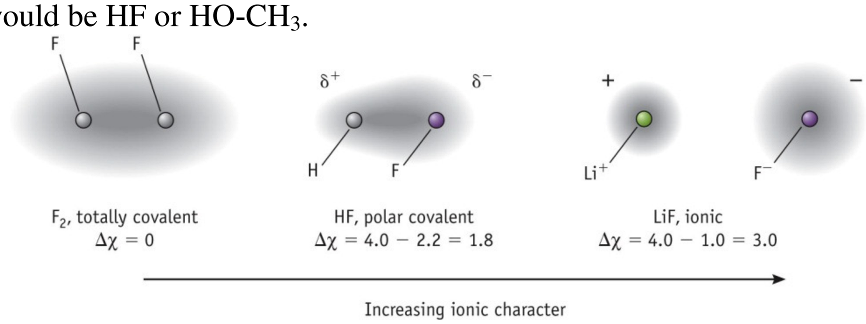



**Bond Polarity and Electronegativity:**

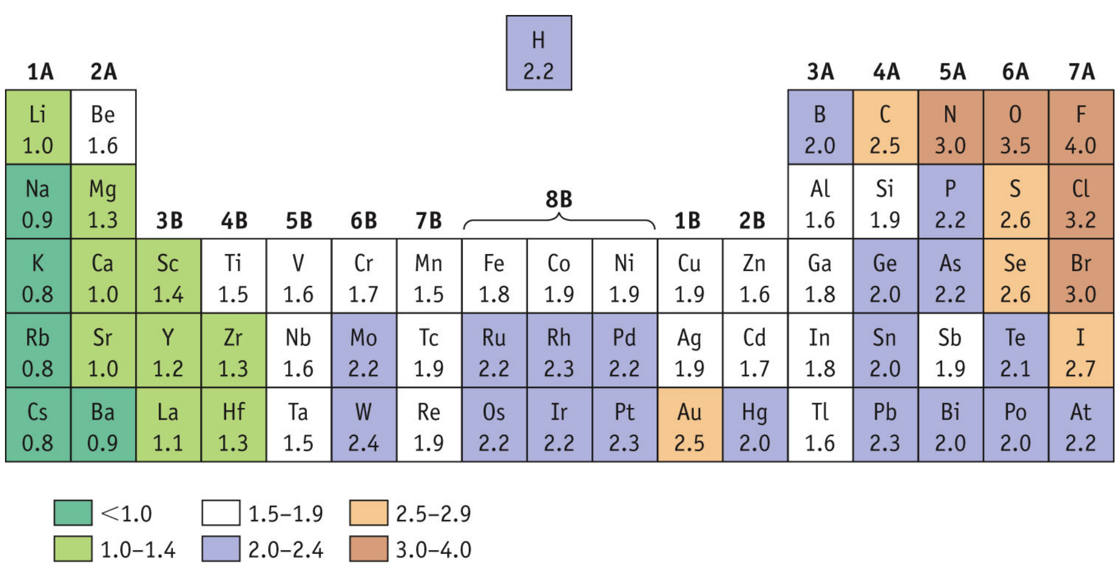
Pure covalent bonding where only two identically atoms are bonded share the electron cloud equally:

$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

When two dissimilar atoms are bonded, the electron cloud is unequally shared. This leads to a **Polar Covalent Bond**. An example would be HF or $HO\text{-}CH_3$.




One end of the molecule will have a partial negative charge and the other a partial positive charge. **Electronegativity**, **X,** is the ability of an atom in a molecule to attract electrons to itself.



- The element with the largest Electronegativity is Fluorine assigned a value of 4.0. The element with the smallest value is Cesium.
- Electronegativity increases going left to right across a period and decreases going down a group.
- Metals have a low Electronegativity < 1 to 2
- Metaloids have a value around 2
- Nonmetals have values greater than 2.

Cesium Fluoride CeF **X** = 4.0 – 0.8 = 3.2 Compound is ionic
Hydrofluoric Acid HF **X** = 4.0 – 2.2 = 1.8 Compound is covalent boind
Because of the difference in Electronegativity for HF, the compound is polar.

**Nonpolar bonds** form when the difference in electronegativity is less than 0.5

**Polar bonds** form when the difference in electronegativity is greater than 0.5

**Ionic bonds** form when the difference in electronegativity is greater than 1.8

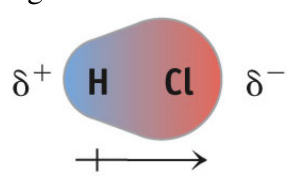
**Ionic Bonds** form between a metal and non metal because the **electronegativity differences are the largest**

**Covalent Bonds** form between two nonmetals because the **electronegativity differences are small**

<u>**Charge Distribution**</u> is the way electrons are distributed in a molecule or ion

- Electroneutrality Principle says electrons will be distributed in such a way that the charges on all atoms are as close to zero as possible
- If a negative charge is present, is should reside on the most electronegative atoms.

<u>**Bond and Molecular Polarity**</u> electron density accumulates toward one side of a molecule giving that side a partially negative, $\delta^-$, or a partial positive charge $\delta^+$.

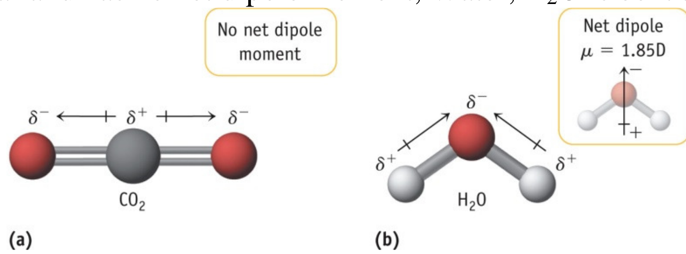



This is measured by **Dipole Moment,** μ, the extent to which the molecules line up in an electric field.

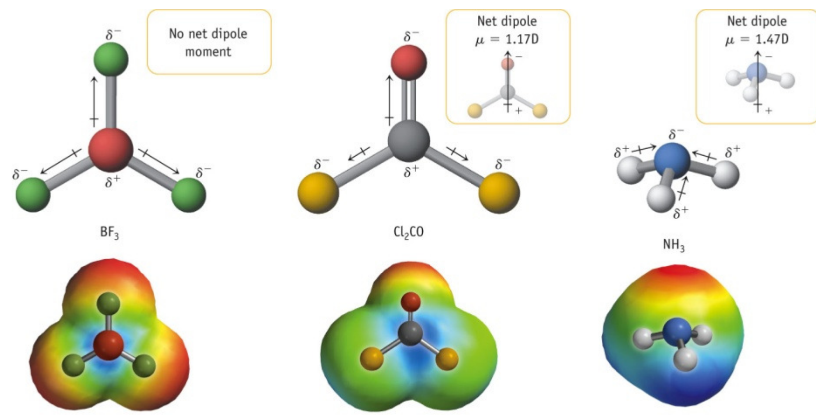
**Table 8.7 Dipole Moments of Selected Molecules**

| Molecule (*AX*) | Moment ($\mu$, D) | Geometry | Molecule ($AX_2$) | Moment ($\mu$, D) | Geometry |
|---|---|---|---|---|---|
| HF | 1.78 | Linear | $H_2O$ | 1.85 | Bent |
| HCl | 1.07 | Linear | $H_2S$ | 0.95 | Bent |
| HBr | 0.79 | Linear | $SO_2$ | 1.62 | Bent |
| HI | 0.38 | Linear | $CO_2$ | 0 | Linear |
| $H_2$ | 0 | Linear | | | |
| **Molecule ($AX_3$)** | **Moment ($\mu$, D)** | **Geometry** | **Molecule ($AX_4$)** | **Moment ($\mu$, D)** | **Geometry** |
| $NH_3$ | 1.47 | Trigonal pyramidal | $CH_4$ | 0 | Tetrahedral |
| $NF_3$ | 0.23 | Trigonal pyramidal | $CH_3Cl$ | 1.92 | Tetrahedral |
| $BF_3$ | 0 | Trigonal planar | $CH_2Cl_2$ | 1.60 | Tetrahedral |
| | | | $CHCl_3$ | 1.04 | Tetrahedral |
| | | | $CCl_4$ | 0 | Tetrahedral |

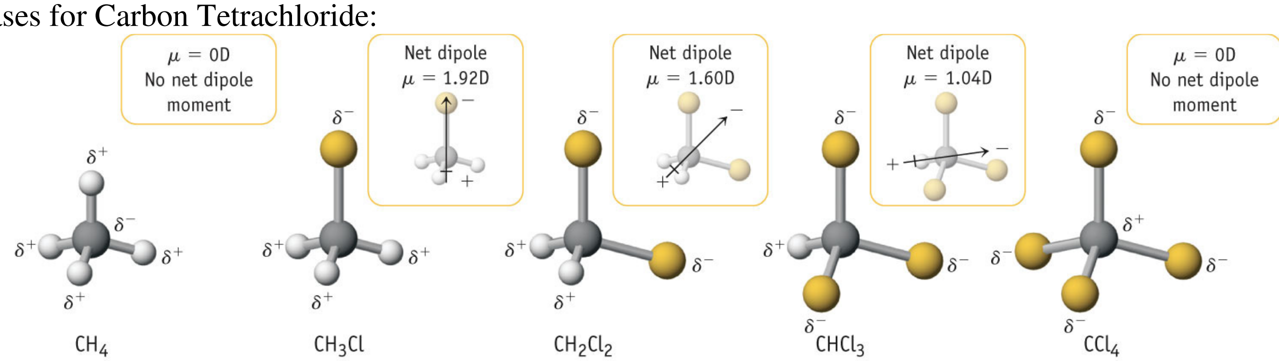
Carbon Dioxide, $CO_2$, is linear and has no net dipole moment, Water, $H_2O$ is bent and has a net dipole moment.




$BF_3$ is trigonal planer so the Electronegativity effect of each Fluorine cancel each other out. $Cl_2CO$ is also trigonal planer, but with the strongly electronegative Chlorine towards one end and less electronegative Oxygen at the other end.




Methane is not polar, but as you replace a Hydrogen with Chlorine, the net dipole moment increases and then decreases for Carbon Tetrachloride:




## 8.9 Bond Order

**The Order of a Bond** is the number of bonding electron pairs shared by two atoms in a molecule.

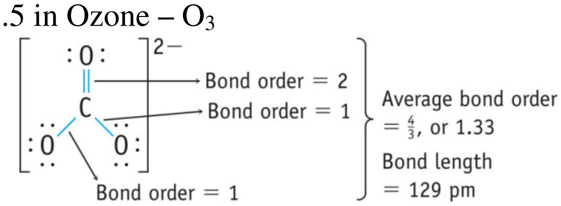
$$\textbf{Bond Order} = \frac{\textbf{\# of shared pairs in all X-Y Bonds}}{\textbf{\# of X-Y links in the molecule or ion}}$$

Bond Order = 1 There is only one single covalent bond between a pair of atoms
$N_2$, $NH_3$, $CH_4$

Bond Order = 2 When 2 electron pairs are shared between atoms
C=O in $CO_2$, C=C in $H_2C{=}CH_2$

Bond Order = 3 When 2 atoms are connected by 3 bonds
C≡O in CO, N≡N in $N_2$

Fractional Bond Order = 1.5 in Ozone – $O_3$



**Bond Length** is the distance between the nuclei of two bonded atoms. It is related to the size of the atoms and the order of the bonds between the two atoms.

**Table 8.8** Some Average Single- and Multiple-Bond Lengths in Picometers (pm)*

| Single Bond Lengths | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Group | | | | | | | | | | | |
| | 1A | 4A | 5A | 6A | 7A | 4A | 5A | 6A | 7A | 7A | 7A |
| | H | C | N | O | F | Si | P | S | Cl | Br | I |
| H | 74 | 110 | 98 | 94 | 92 | 145 | 138 | 132 | 127 | 142 | 161 |
| C | | 154 | 147 | 143 | 141 | 194 | 187 | 181 | 176 | 191 | 210 |
| N | | | 140 | 136 | 134 | 187 | 180 | 174 | 169 | 184 | 203 |
| O | | | | 132 | 130 | 183 | 176 | 170 | 165 | 180 | 199 |
| F | | | | | 128 | 181 | 174 | 168 | 163 | 178 | 197 |
| Si | | | | | | 234 | 227 | 221 | 216 | 231 | 250 |
| P | | | | | | | 220 | 214 | 209 | 224 | 243 |
| S | | | | | | | | 208 | 203 | 218 | 237 |
| Cl | | | | | | | | | 200 | 213 | 232 |
| Br | | | | | | | | | | 228 | 247 |
| I | | | | | | | | | | | 266 |

| Multiple Bond Lengths | | | |
|---|---|---|---|
| C=C | 134 | C≡C | 121 |
| C=N | 127 | C≡N | 115 |
| C=O | 122 | C≡O | 113 |
| N=O | 115 | N≡O | 108 |

*1 pm = $10^{-12}$ m.

The average C-H bond length is 110 pm. The C-H bond in Methane, $CH_4$, is 109.4 pm, in Acetylene, H-C≡C-H is 105.9 pm. The H-X distance in hydrogen halides increases in order predicted by the halogen size of H-F < H-Cl < H-Br < H-I.

**Bond Dissociation Enthalpy is** the enthalpy change for breaking a bond in a molecule with the reactants and products in the gas phase.
The process of breaking bonds in a molecule is always endothermic, ΔH is +.
The formation of bonds from atoms or radicals in the gas phase is always exothermic, ΔH is -.