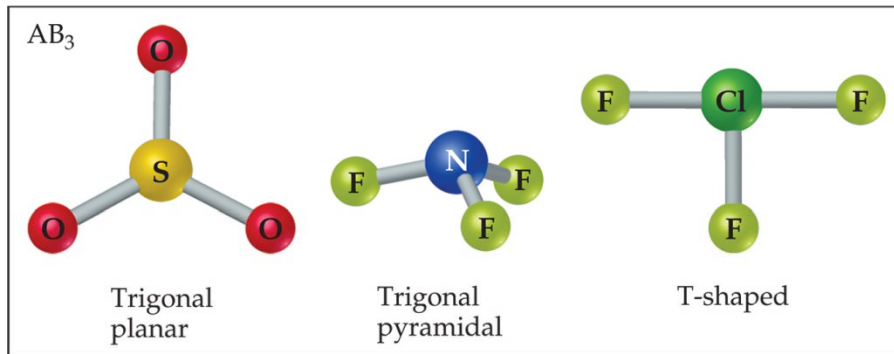
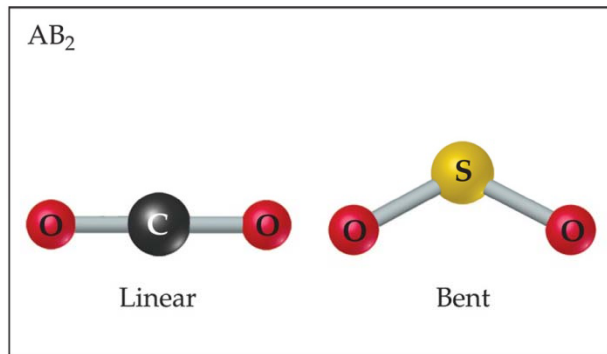


# **Concepts of Chemical Bonding and Molecular Geometry Part 2**

**David A. Katz  
Pima Community College  
Tucson, AZ**

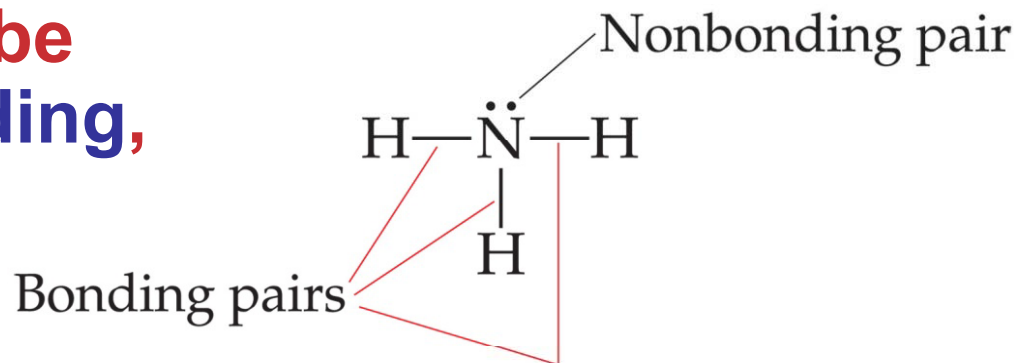
# Molecular Shapes



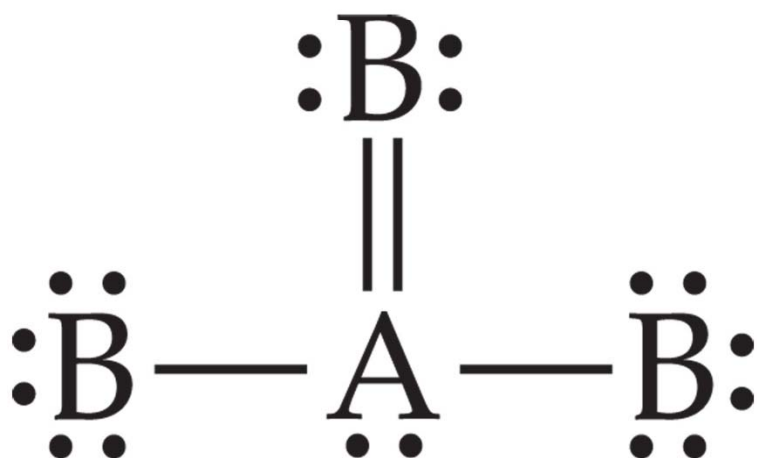
- The shape of a molecule plays an important role in its reactivity.
- By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.

# What Determines the Shape of a Molecule?

- Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.
- By assuming the *electron pairs are placed as far as possible from each other*, we can predict the shape of the molecule.



# Electron Pair Geometry



This molecule has four electron pair domains: two single bonds, one double bond, and one nonbonded electron pair

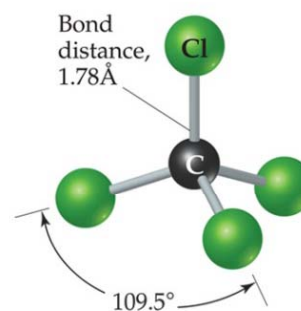
- We sometimes refer to the electron pairs as **electron pair domains**.
- A single bond is one electron pair.
- A double or triple bond shared between two atoms counts as one electron pair domain.
- A nonbonded electron pair counts as one electron pair.

# Valence Shell Electron Pair Repulsion Theory (VSEPR)

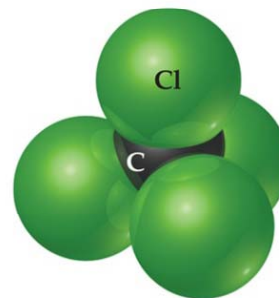
*“The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.”*



(a)



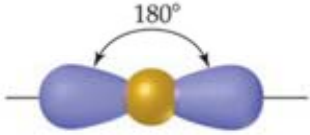
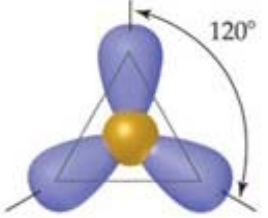
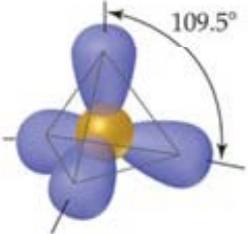
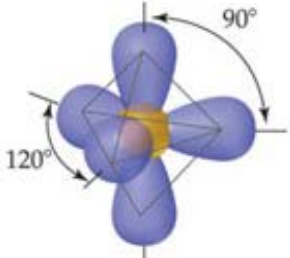
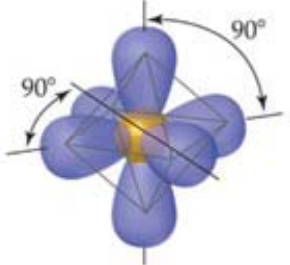
(b)



(c)

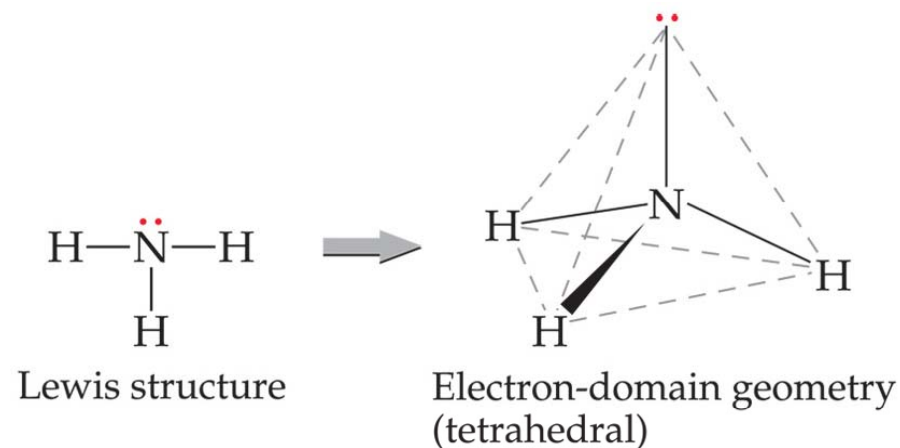
# Electron-Pair Geometries

These are the electron-pair geometries for two through six electron pairs around a central atom.

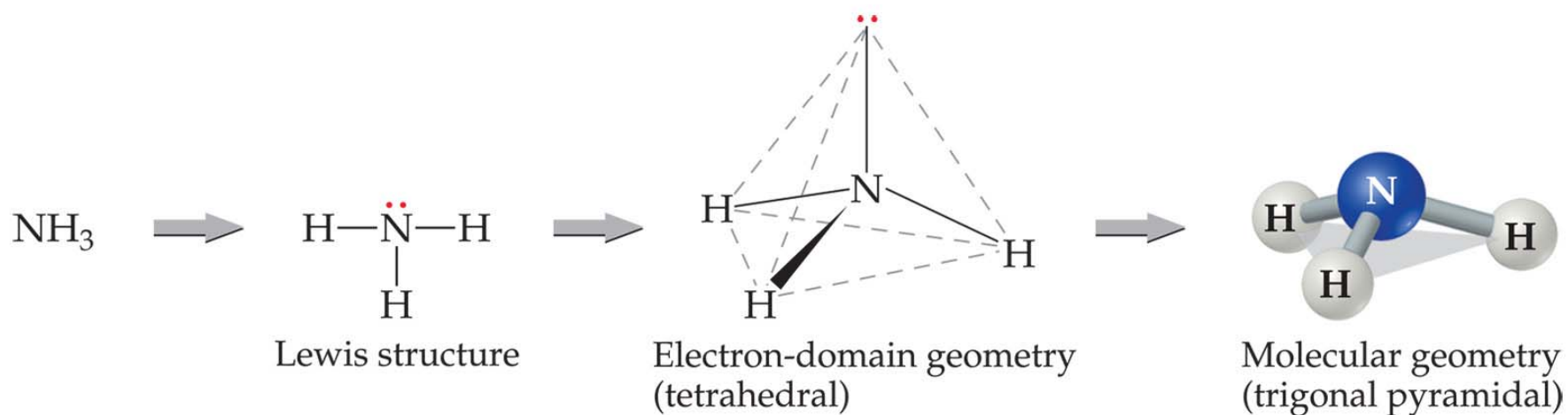
Number of electron pairs	Arrangement of electron pairs	Electron pair geometry	Predicted bond angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

# Electron Pair Geometries

- All one must do is count the number of electron pair domains in the Lewis structure.
- The geometry will be that which corresponds to that number of electron pairs



# Molecular Geometries

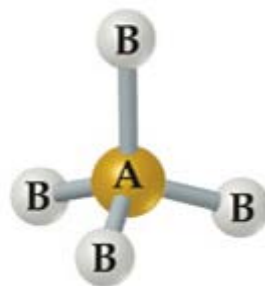


- The electron pair geometry is often NOT the shape of the molecule.
- The molecular geometry is defined by the positions of the atoms in the molecules, not the nonbonding pairs.

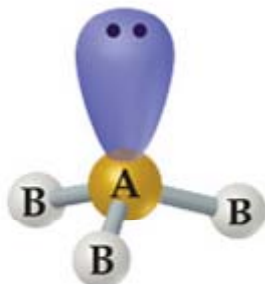
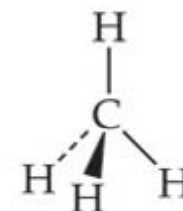


# Molecular Geometries

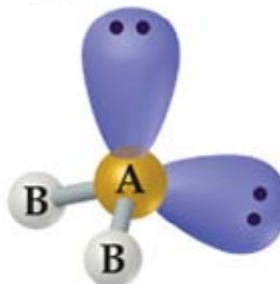
Within each electron pair domain, there might be more than one molecular geometry.



Tetrahedral





Trigonal pyramidal



Bent



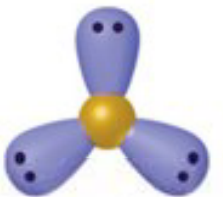
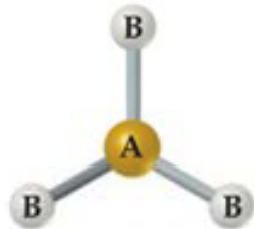
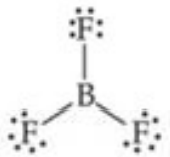
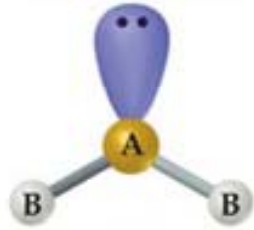
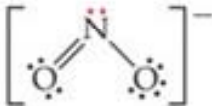
# Linear Electron Domain

Number of electron pairs	Electron pair geometry	Number of bonds	Number of nonbonded pairs	Molecular geometry	Examples
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$ Cl-Be-Cl

- In this domain, there is only one molecular geometry: linear.
- The bond angle is  $180^\circ$
- Any element in Group IIA with 2 single bonds is linear.


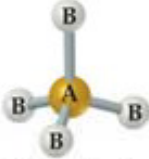
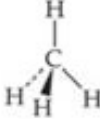
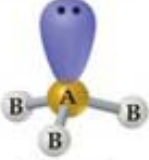
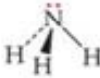
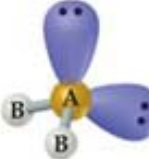

**NOTE:** If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

# Trigonal Planar or Triangular Electron Domain

Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

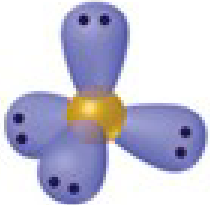
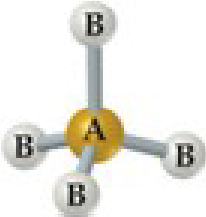
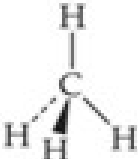
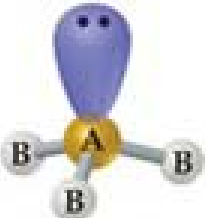

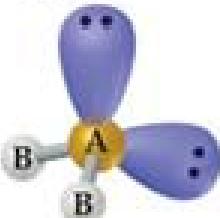

- There are two molecular geometries:
  - **Trigonal planar**, if there are three single bonds: Group IIIA elements with three single bonds are triangular.
  - **Bent**, if one of the domains is a nonbonding pair.

# Tetrahedral Electron Domain

Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

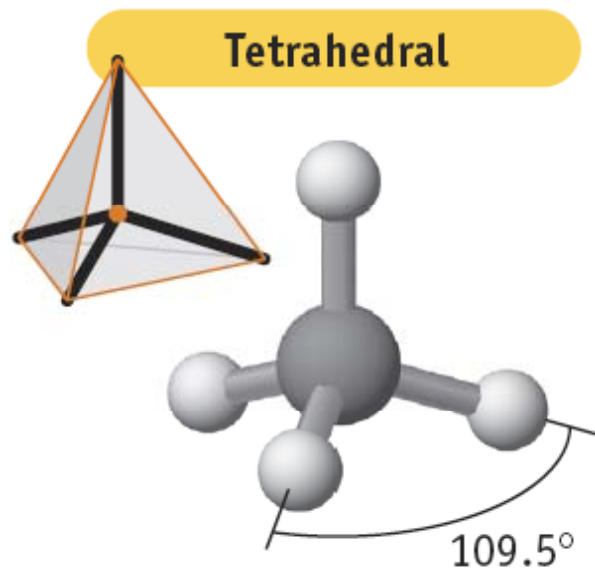
- There are three molecular geometries:
  - **Tetrahedral**, if there are 4 bonding pairs: Group IVA elements
  - **Trigonal pyramidal** there are three bonding pairs and one nonbonding pair: Group VA elements
  - **Bent** if there are two bonding pairs and two nonbonding pairs: Group VIA elements

# Tetrahedral Electron Domain

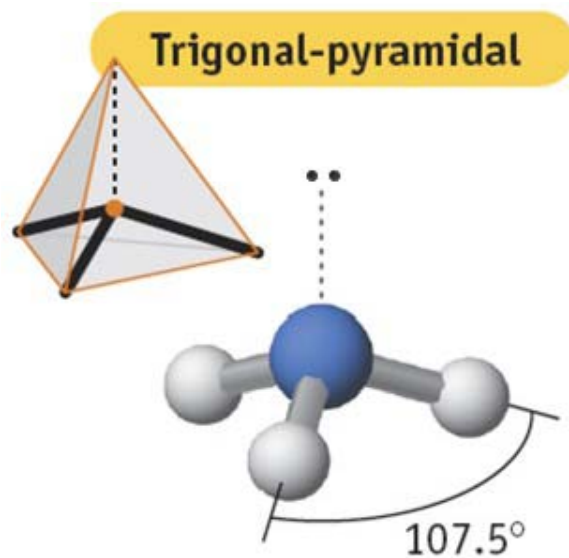
Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

# Tetrahedral Electron Domain

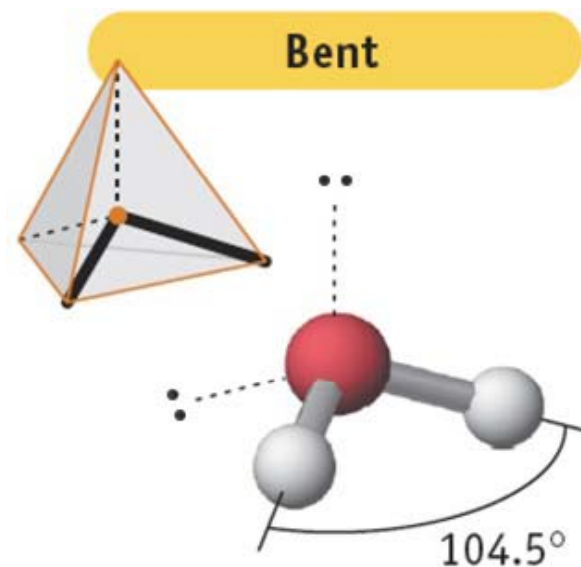
## Three important molecules



**Methane, CH<sub>4</sub>**  
4 bond pairs  
no lone pairs



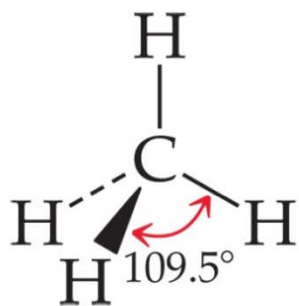
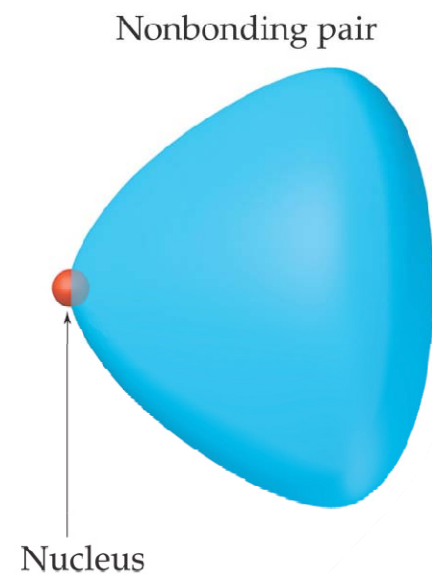
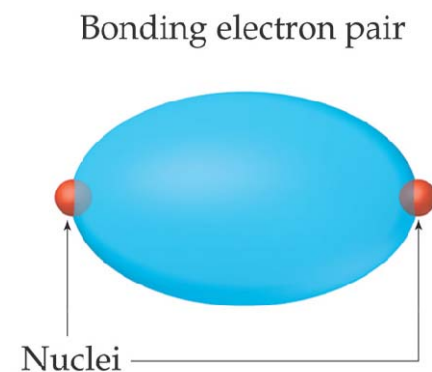
**Ammonia, NH<sub>3</sub>**  
3 bond pairs  
1 lone pair



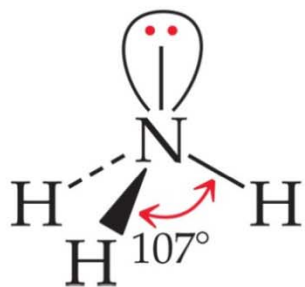
**Water, H<sub>2</sub>O**  
2 bond pairs  
2 lone pairs

# Nonbonding Pairs and Bond Angle

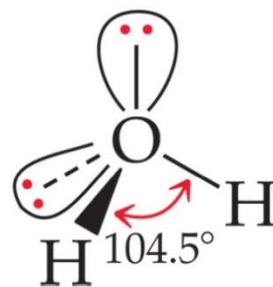
- The electron densities of nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.



methane

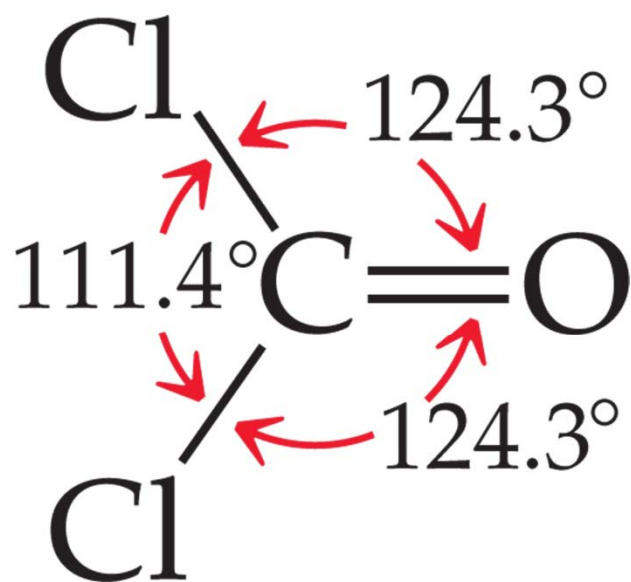


ammonia



water

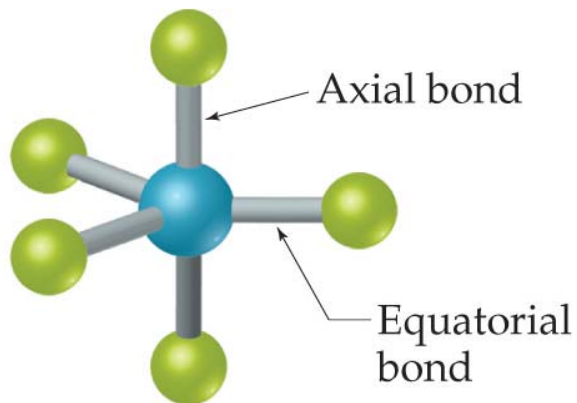
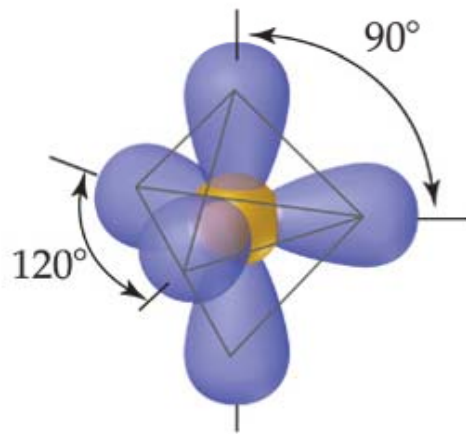
# Multiple Bonds and Bond Angles



- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.



# Trigonal Bipyramidal Electron Domain



- There is no equiangular arrangement for five bonds to a central atom.
- There are two distinct positions in this geometry:
  - **Axial:** 180° bond angle
  - **Equatorial:** 120° bond angle
- To compensate for the smaller bond angle between the axial and equatorial planes (90°), the bond distances of the axial bonds are longer than the bond distances of the equatorial bonds.

# Trigonal Bipyramidal Electron Domain

- There are four distinct molecular geometries in this domain:

- **Trigonal bipyramidal:**

5 single bonds

- **Seesaw:**



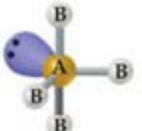
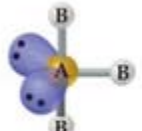

4 single bonds,  
1 nonbonded electron pair

- **T-shaped:**


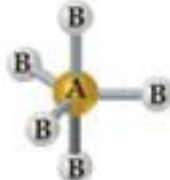
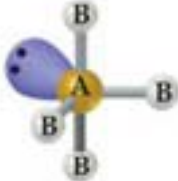
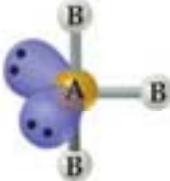

3 single bonds,  
2 nonbonded electron pairs

- **Linear:**

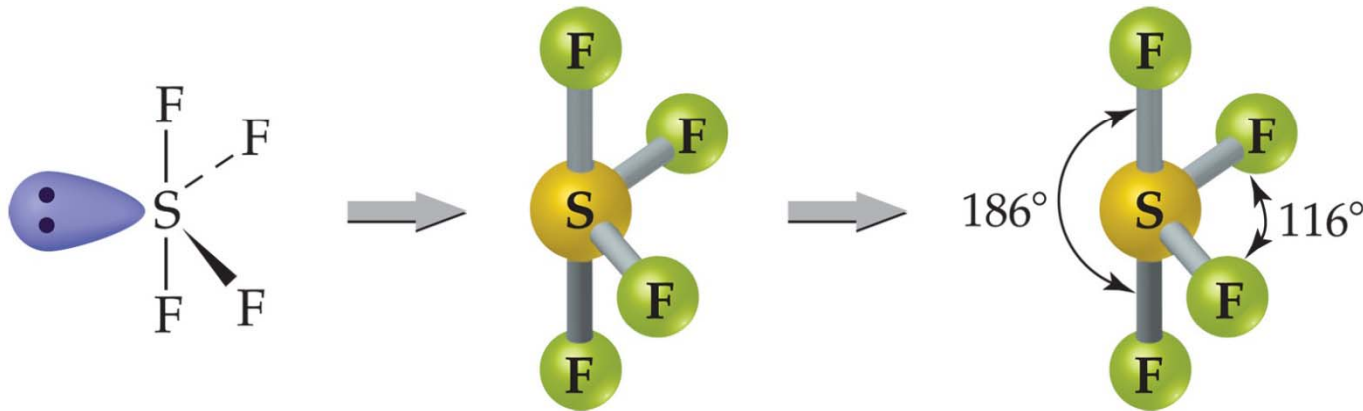
2 single bonds,  
3 nonbonded electron pairs

Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl <sub>5</sub>
		4	1	 Seesaw	SF <sub>4</sub>
		3	2	 T-shaped	ClF <sub>3</sub>
		2	3	 Linear	XeF <sub>2</sub>

# Trigonal Bipyramidal Electron Domain

Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	$\text{PCl}_5$
		4	1	 Seesaw	$\text{SF}_4$
		3	2	 T-shaped	$\text{ClF}_3$
		2	3	 Linear	$\text{XeF}_2$

# Trigonal Bipyramidal Electron Domain



**Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.**

**The F-S-F axial bond angle is 186° instead of 180°.  
The F-S-F equatorial bond angle is 116° instead of 120°.**

# Octahedral Electron Domain

- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:

- **Octahedral:**



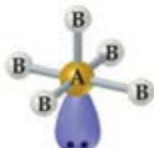
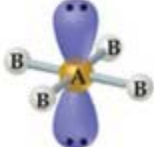
6 single bonds

- **Square pyramidal:**

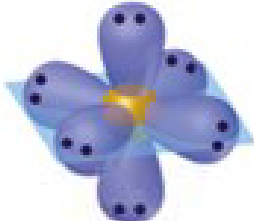
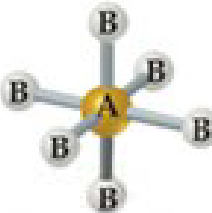
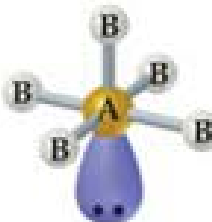
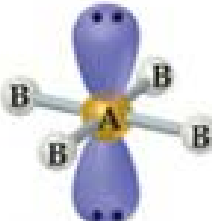
5 single bonds,  
1 nonbonded electron pair

- **Square planar:**

4 single bonds,  
2 nonbonded electron pairs

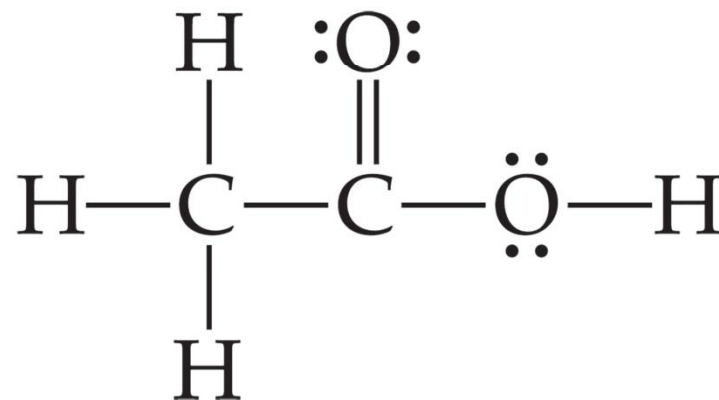
Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
6	 Octahedral	6	0	 Octahedral	SF <sub>6</sub>
		5	1	 Square pyramidal	BrF <sub>5</sub>
		4	2	 Square planar	XeF <sub>4</sub>

# Octahedral Electron Domain

Number of electron pairs	Electron pair Geometry	Number of bonds	Number of nonbonded electron pairs	Molecular geometry	Examples
6	 Octahedral	6	0	 Octahedral	$\text{SF}_6$
		5	1	 Square pyramidal	$\text{BrF}_5$
		4	2	 Square planar	$\text{XeF}_4$

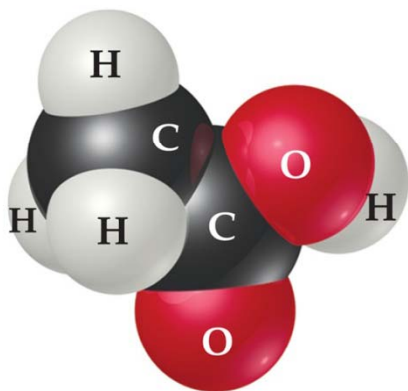
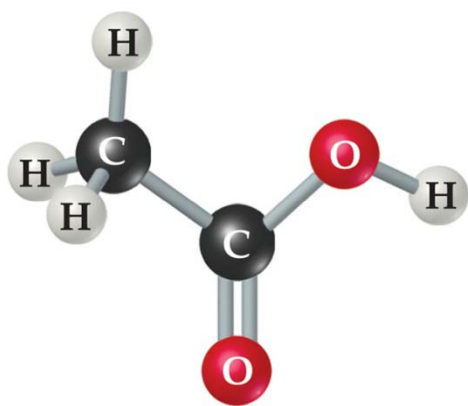
# Larger Molecules

In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.



	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}- \\    \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \text{:O:} \\     \\  \text{C}  \end{array}  $	$  \begin{array}{c}  \ddot{\text{O}}-\text{H}  \end{array}  $
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

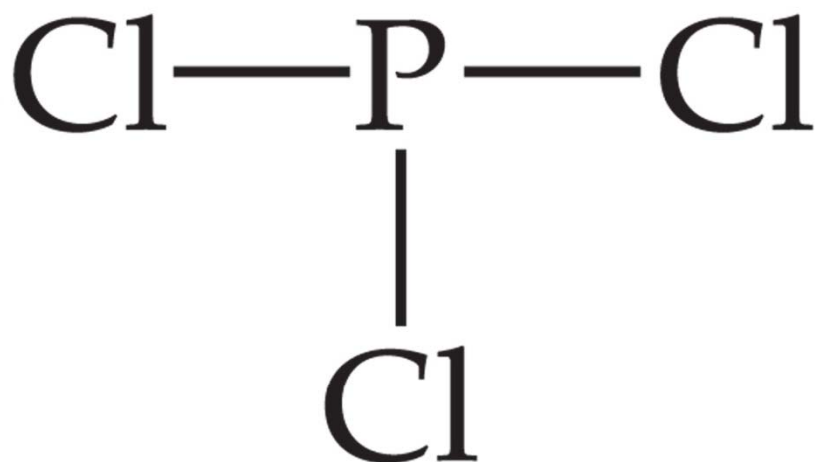
# Larger Molecules



**This approach makes sense, especially because larger molecules tend to react at a particular site in the molecule.**



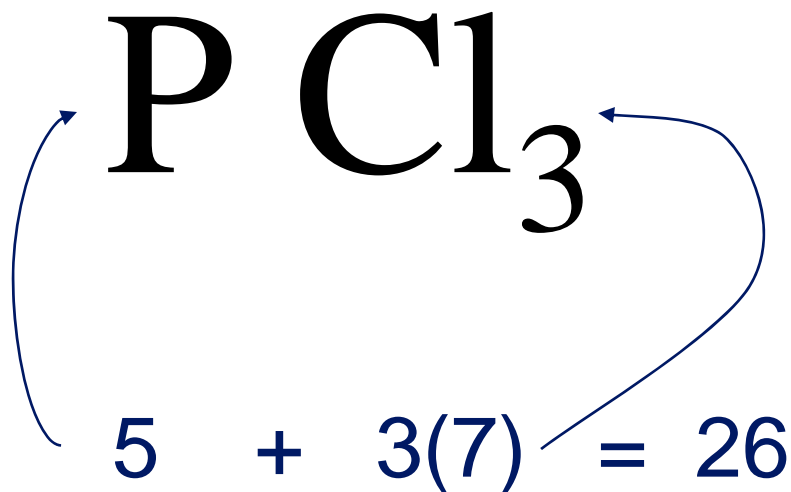
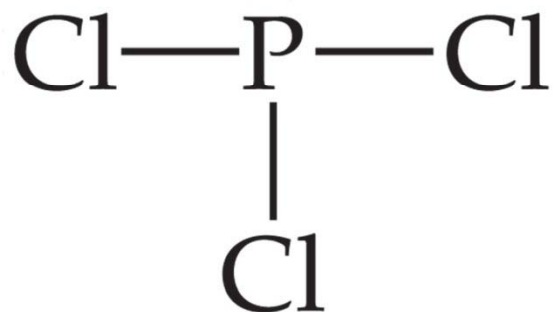
# Writing Lewis Structures



1. Draw the structure of the molecule using the VSEPR Theory.

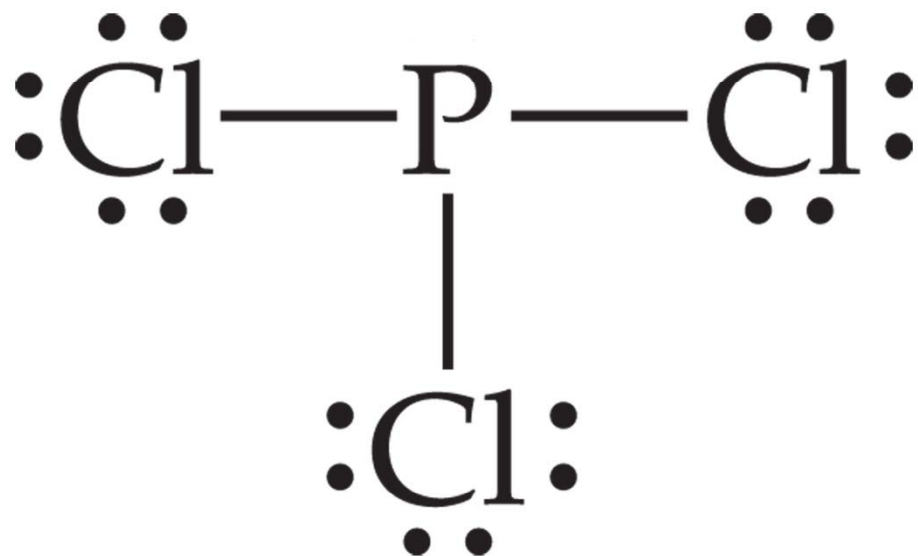
Remember, the central atom is the *least* electronegative element that isn't hydrogen. (It is usually the element that comes first in the chemical formula.)

# Writing Lewis Structures



2. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
  - If it is an anion, add one electron for each negative charge.
  - If it is a cation, subtract one electron for each positive charge.

# Writing Lewis Structures

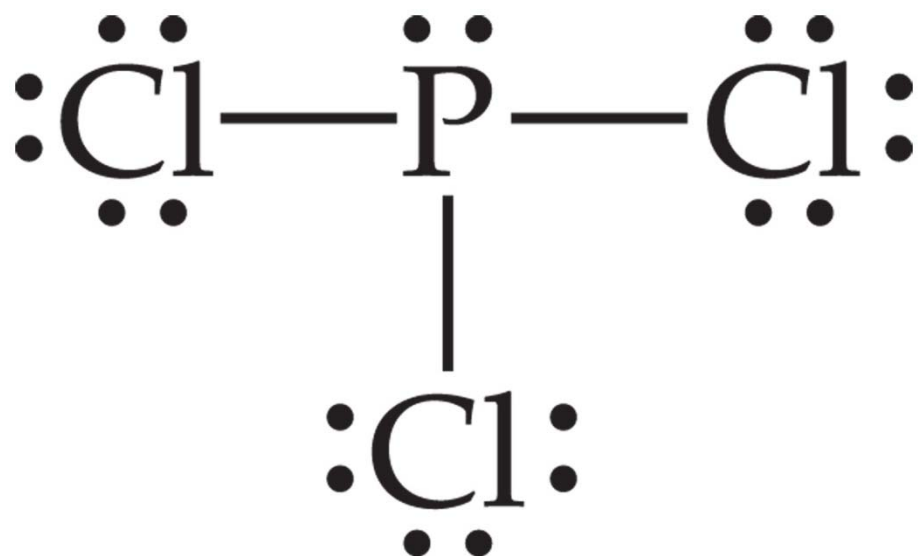


**3. Fill the octets of the outer atoms.**

**Keep track of the electrons:**

$$26 - 6 \text{ (for three bonds)} = 20 - 3(6) \text{ (for 3 chlorines)} = 2$$

# Writing Lewis Structures



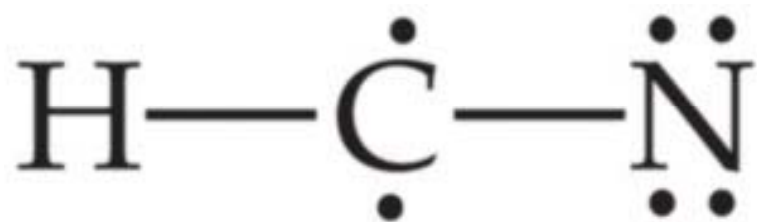
4. Fill the octet of the central atom.

(in this example, the phosphorus atom)

Keep track of the electrons:

$$26 - 6 = 20 - 3(6) = 2 - 2 = 0$$

# Writing Lewis Structures



5. If you run out of electrons before the central atom has an octet...

...form multiple bonds until it does.



# Writing Lewis Structures

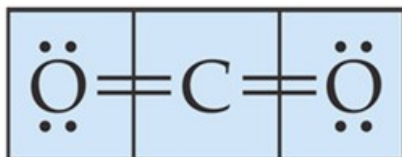
## 6. Assign formal charges.

- a) For each atom, count the number of valence electrons normally assigned to that unbonded atom.
- b) For each atom, count the electrons in lone pairs assigned to that atom in the Lewis structure.  
Add to that, **one-half** of the electrons in the bonds it shares with other atoms. (For a single bond, 1 electron; for a double bond, 2 electrons, etc.)
- c) Subtract the number of assigned electrons from the number of valence electrons for each atom. The difference is its formal charge.

# Writing Lewis Structures

## 6. Assigning formal charges (continued)

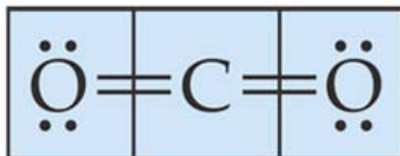
As an example, we will consider two possible structures for  $\text{CO}_2$  :



- a) An oxygen atom normally has 6 valence electrons.
- b) Each oxygen in this structure has 2 lone pairs assigned to it = 4 electrons.  
Each oxygen has a double bond =  $\frac{1}{2} \times 4$  electrons = 2  
The total number of assigned electrons = 6
- c) Formal charge = 6 valence electrons – 6 assigned electrons  
= 0 for each oxygen

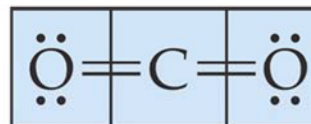
# Writing Lewis Structures

## 6. Assigning formal charges (continued)



- a) A carbon atom normally has 4 valence electrons.
- b) There are no lone pairs assigned to the carbon.  
The carbon has two double bonds =  $\frac{1}{2} \times 4 \text{ electrons} \times 2 = 4$   
The total number of assigned electrons = 4
- c) Formal charge = 4 valence electrons – 4 assigned electrons  
= 0 for carbon

In summary:



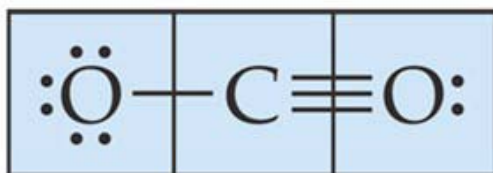
Valence electrons:	6	4	6
–(Electrons assigned to atom):	6	4	6
<hr/>			
Formal charge:	0	0	0



# Writing Lewis Structures

## 6. Assigning formal charges (continued)

Repeat the process for the second structure:

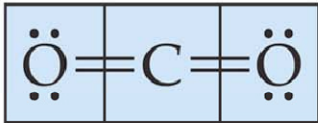
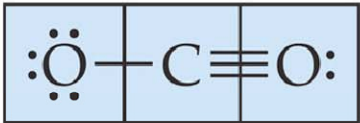


The results are shown in the table below:

	<table border="1"><tr><td><math>\ddot{\text{O}}\text{=}</math></td><td><math>\text{C=}</math></td><td><math>\ddot{\text{O}}\text{:}</math></td></tr></table>	$\ddot{\text{O}}\text{=}$	$\text{C=}$	$\ddot{\text{O}}\text{:}$	<table border="1"><tr><td><math>\text{:}\ddot{\text{O}}\text{—}</math></td><td><math>\text{C}\equiv</math></td><td><math>\text{O:}</math></td></tr></table>	$\text{:}\ddot{\text{O}}\text{—}$	$\text{C}\equiv$	$\text{O:}$
$\ddot{\text{O}}\text{=}$	$\text{C=}$	$\ddot{\text{O}}\text{:}$						
$\text{:}\ddot{\text{O}}\text{—}$	$\text{C}\equiv$	$\text{O:}$						
Valence electrons:	6    4    6	6    4    6						
–(Electrons assigned to atom):	6    4    6	7    4    5						
Formal charge:	0    0    0	–1    0    +1						

# Writing Lewis Structures

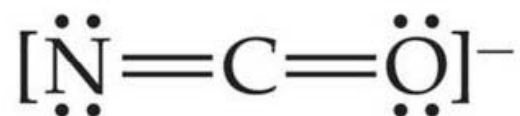
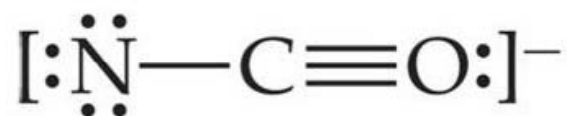
- The best Lewis structure...
  - ...is the one with the fewest charges.
  - ...puts a negative charge on the most electronegative atom.

		
Valence electrons:	6    4    6	6    4    6
-(Electrons assigned to atom):	6    4    6	7    4    5
Formal charge:	0    0    0	-1    0    +1

The first Lewis structure,  $\text{O}=\text{C}=\text{O}$ , is preferred because it is the one with the fewest charges.

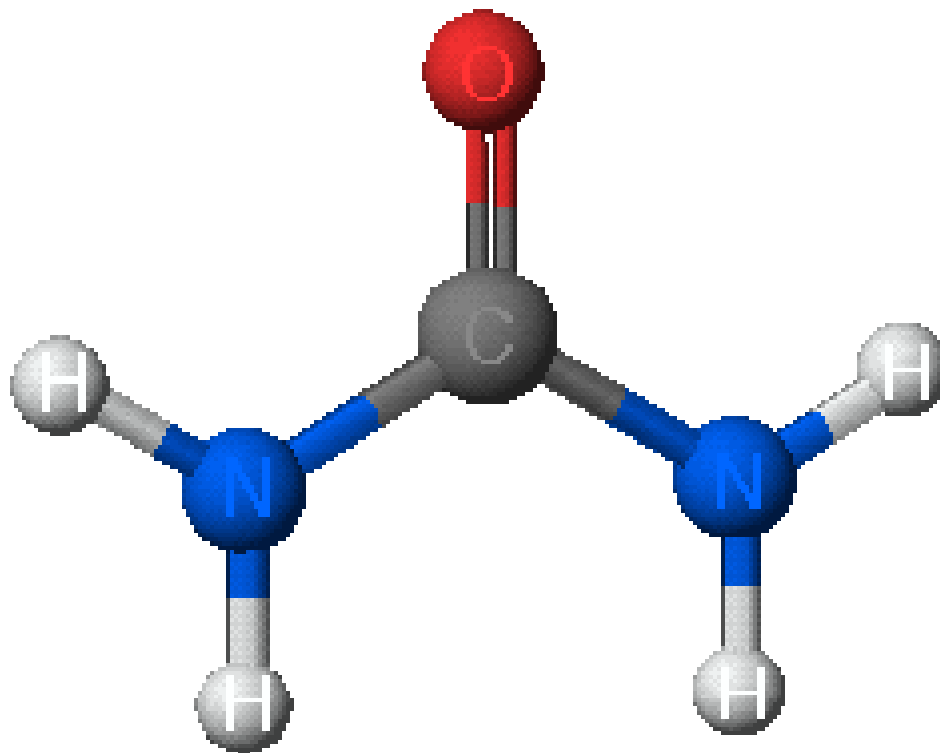
# Writing Lewis Structures

- Which is the best Lewis structure for the thiocyanate ion, shown below?



# Writing Lewis Structures

Urea,  $(\text{NH}_2)_2\text{CO}$

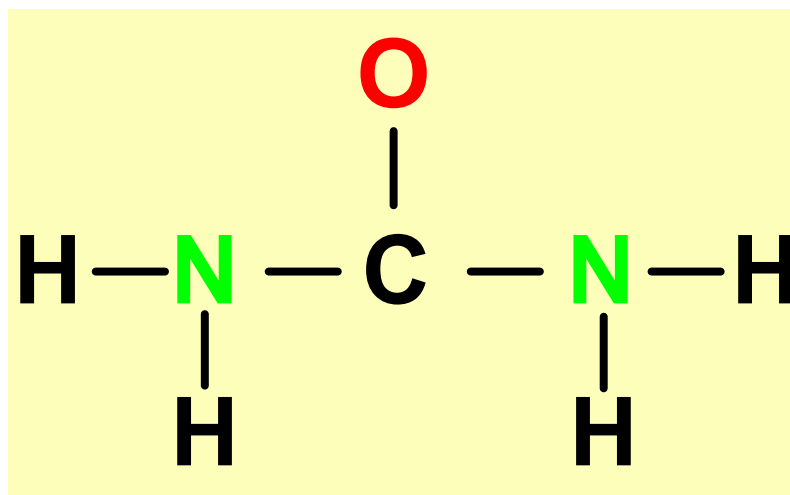


# Writing Lewis Structures

## Urea, $(\text{NH}_2)_2\text{CO}$

1. Number of valence electrons = 24 e<sup>-</sup>
2. Draw sigma bonds

There are 7 bonds:  $7 \times 2 = 14 \text{ e}^-$



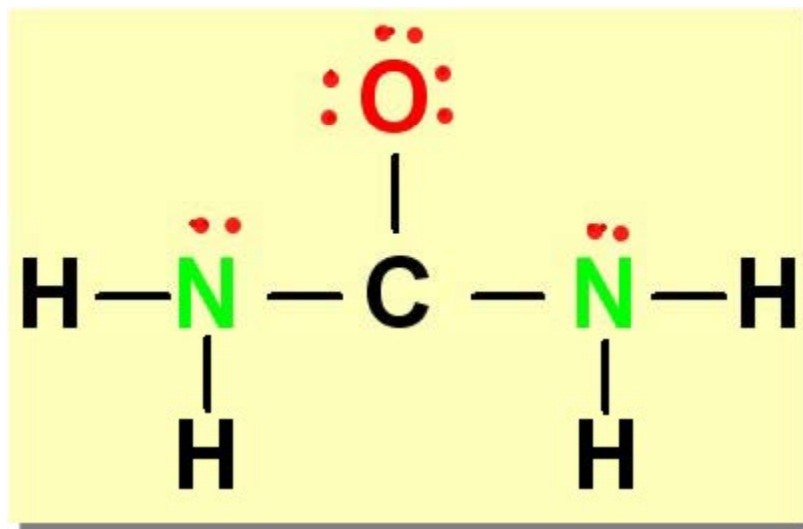
# Writing Lewis Structures

## Urea, $(\text{NH}_2)_2\text{CO}$

3. Place remaining electron pairs in the molecule

Each nitrogen needs a pair of non-bonded  $e^-$

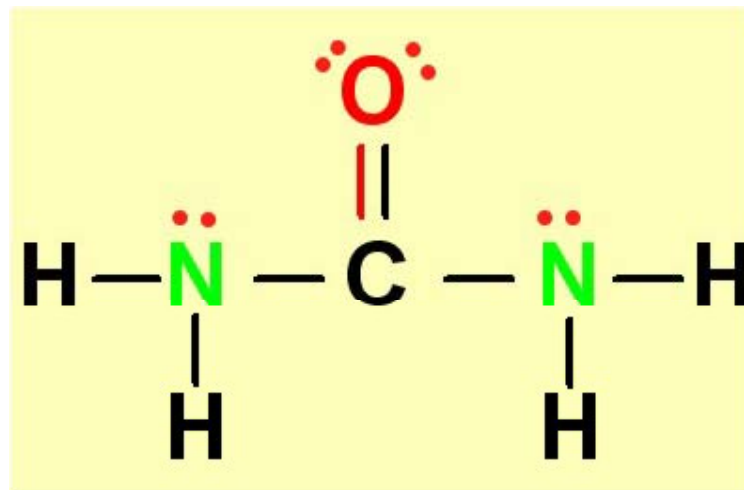
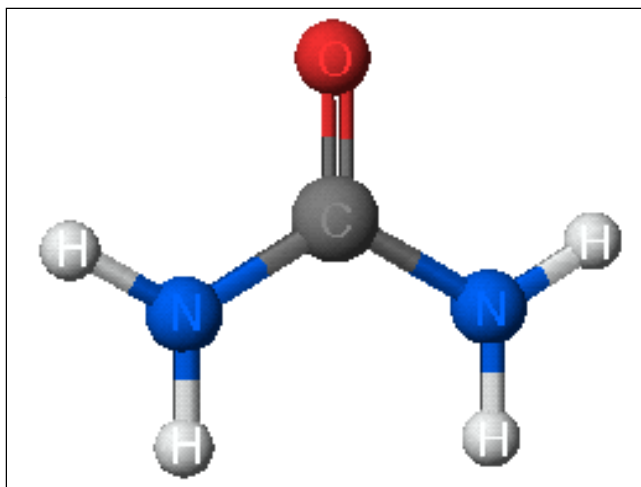
Oxygen needs 6  $e^-$  to complete its octet



# Writing Lewis Structures

## Urea, $(\text{NH}_2)_2\text{CO}$

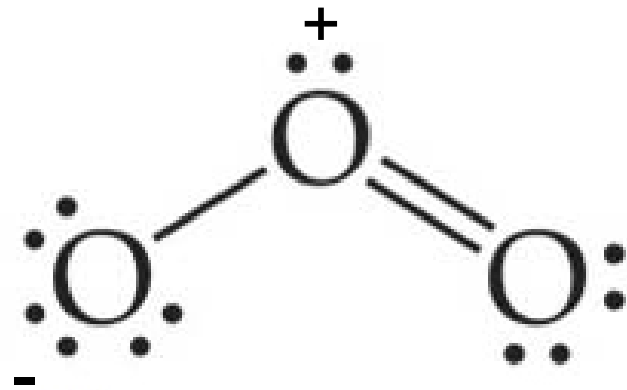
4. Complete octet on C atom with double bond.



bonds:  $8 \times 2 = 16 \text{ e}^-$  (includes double bond) +  $4 \text{ e}^-$  (nitrogens)  
+  $4 \text{ e}^-$  (oxygen) =  $24 \text{ e}^-$

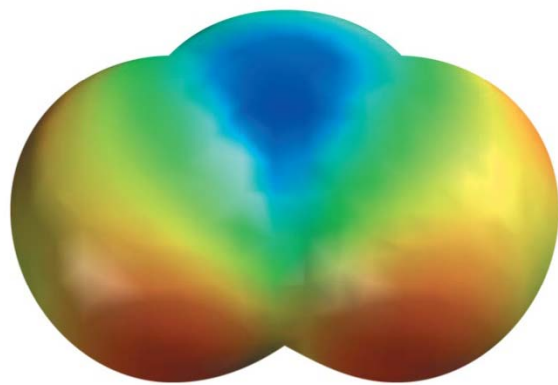
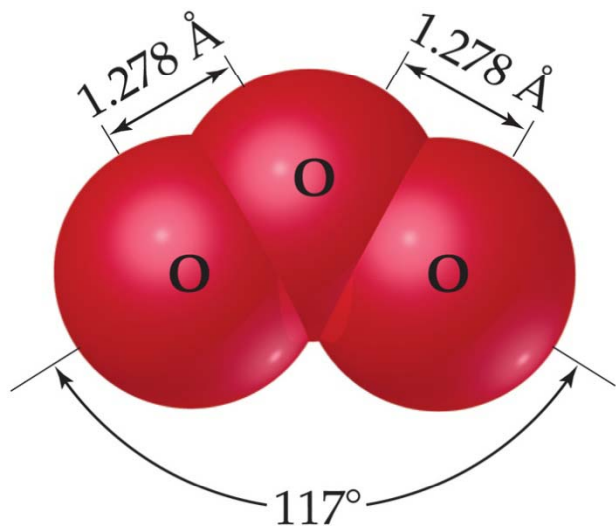
# Resonance

This is the Lewis structure we would draw for ozone,  $O_3$ .





# Resonance

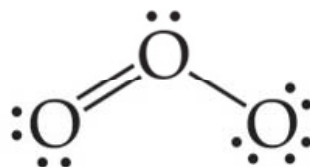


- But this is at odds with the true, observed structure of ozone, in which...
  - ...both O—O bonds are the same length.
  - ...both outer oxygens have a charge of  $-1/2$ .

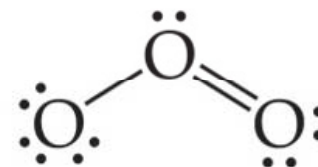
# Resonance

- One Lewis structure cannot accurately depict a molecule such as ozone.
- We use multiple structures, which we call resonance structures, to describe the molecule.

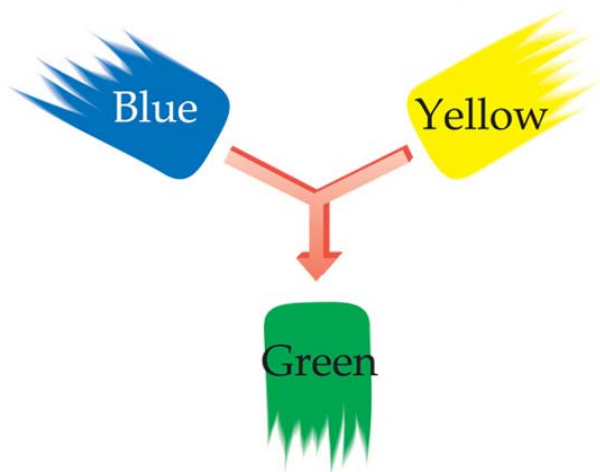
Resonance structure



Resonance structure



Primary color    Primary color

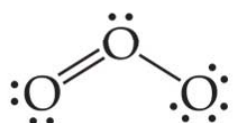


# Resonance

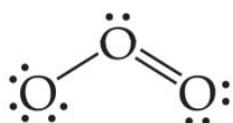
Just as green is a synthesis of blue and yellow...

...ozone is a synthesis of these two resonance structures.

Resonance structure



Resonance structure



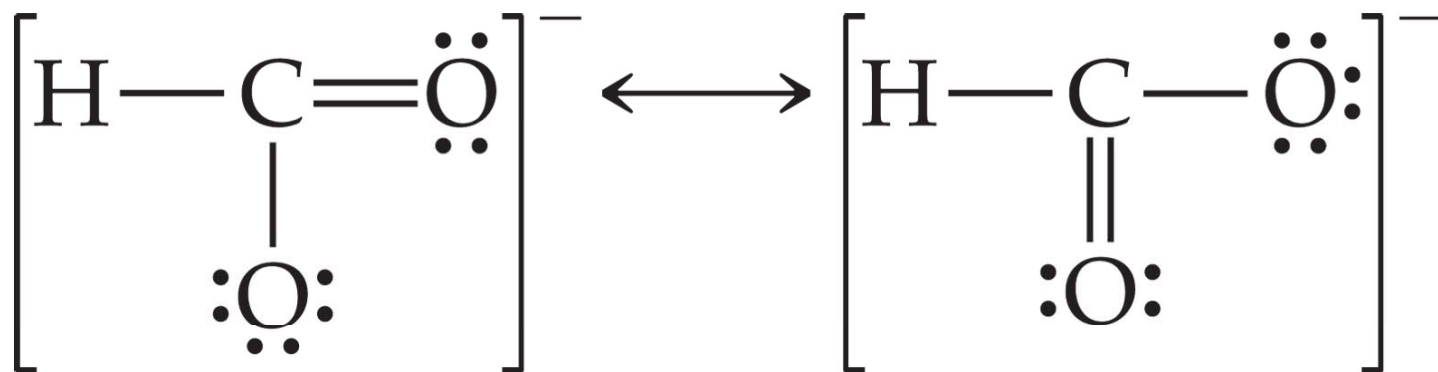
Ozone molecule

Ozone molecule

The actual ozone structure is called a resonance hybrid of the two structures.

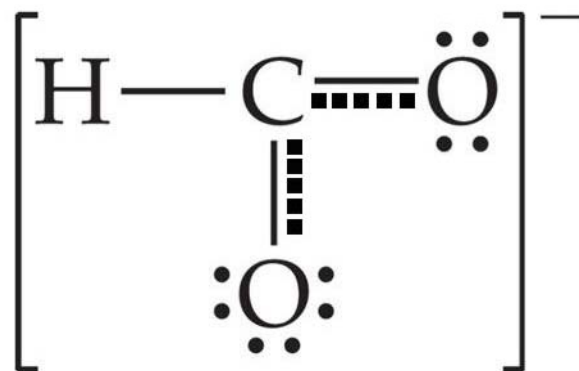
# Resonance

- Shown below are the resonance structures for the formate ion,  $\text{HCO}_2^-$
- In truth, the electrons that form the second C—O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.
- They are not **localized**, but rather are **delocalized**.



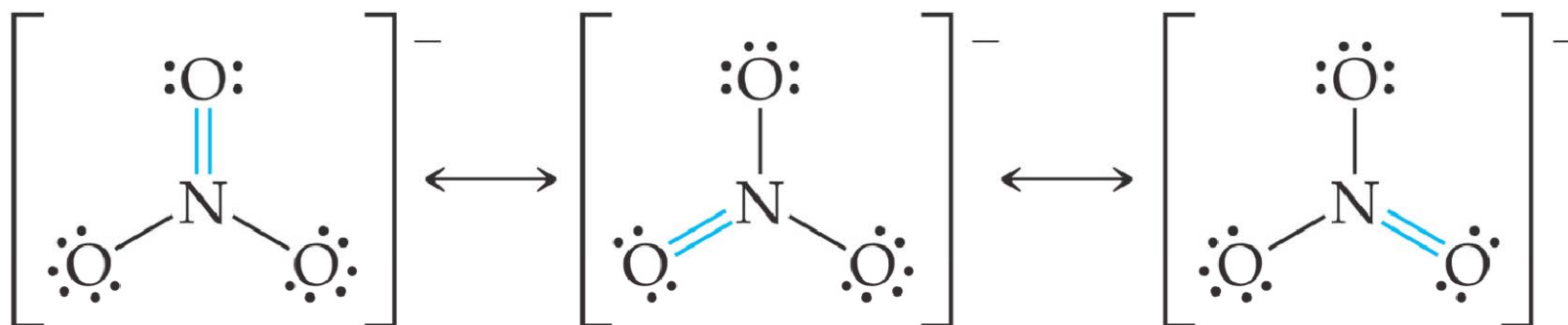
# Resonance

- The delocalized electrons would be represented on the diagram by a dashed line:



# Delocalized Electrons: Resonance

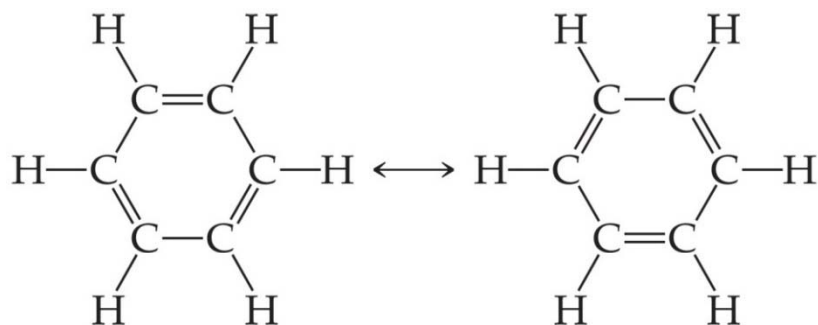
When writing Lewis structures for species like the nitrate ion,  $\text{NO}_3^-$ , resonance structures more accurately reflect the structure of the ion.



The actual structure of the nitrate ion is a resonance hybrid of the three structures.

Similar diagrams are used for species such as carbonate,  $\text{CO}_3^{2-}$ , sulfite,  $\text{SO}_3^{2-}$ , and formate,  $\text{HCO}_2^-$

# Resonance



- The organic compound benzene, C<sub>6</sub>H<sub>6</sub>, has two simple resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.



# Exceptions to the Octet Rule

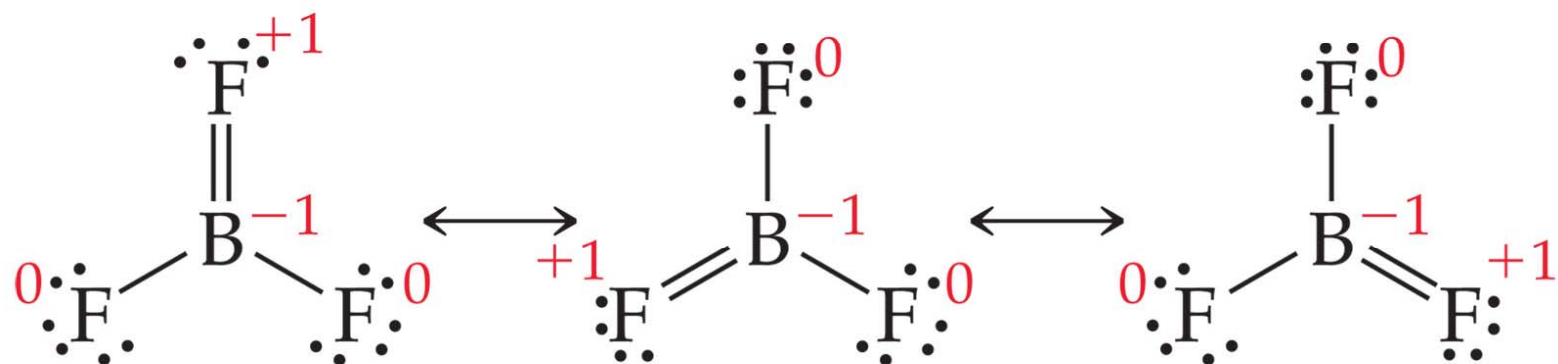
- **There are three types of ions or molecules that do not follow the octet rule:**
  - **Ions or molecules with an odd number of electrons.**
  - **Ions or molecules with less than an octet.**
  - **Ions or molecules with more than eight valence electrons (an expanded octet).**



# Odd Number of Electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

# Fewer Than Eight Electrons

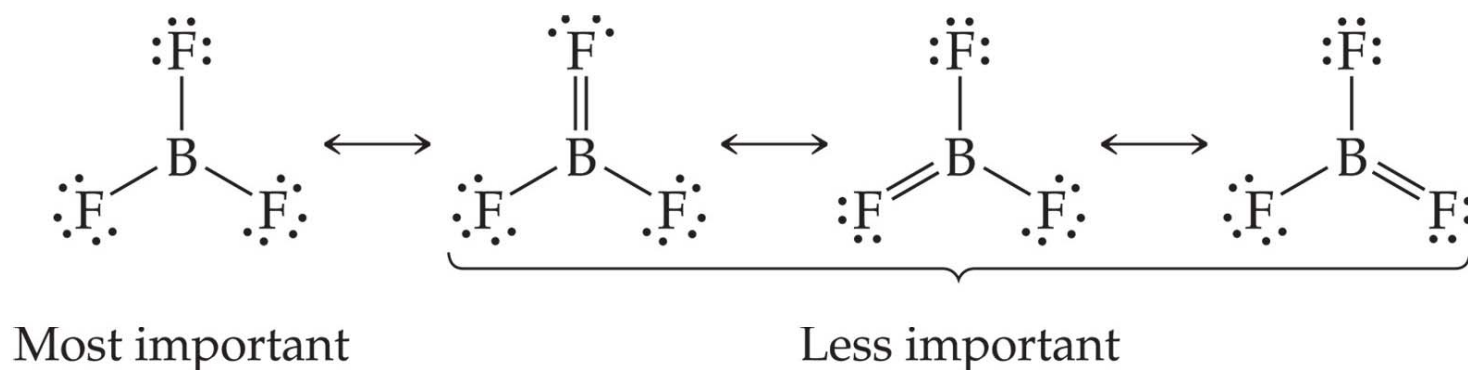


- **Consider  $\text{BF}_3$ :**

- Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
- This would not be an accurate picture of the distribution of electrons in  $\text{BF}_3$ .

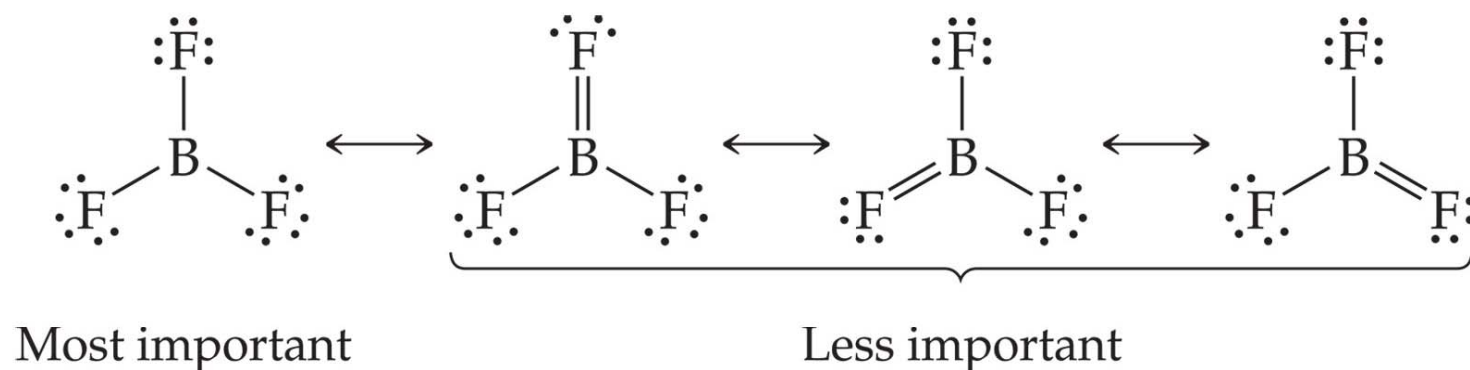
# Fewer Than Eight Electrons

Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.

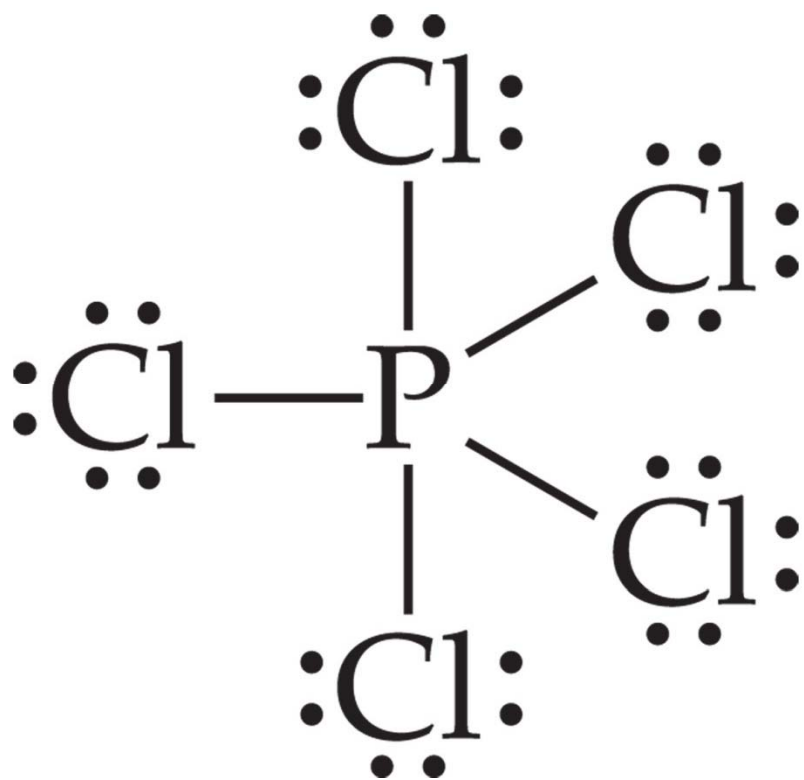


# Fewer Than Eight Electrons

The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



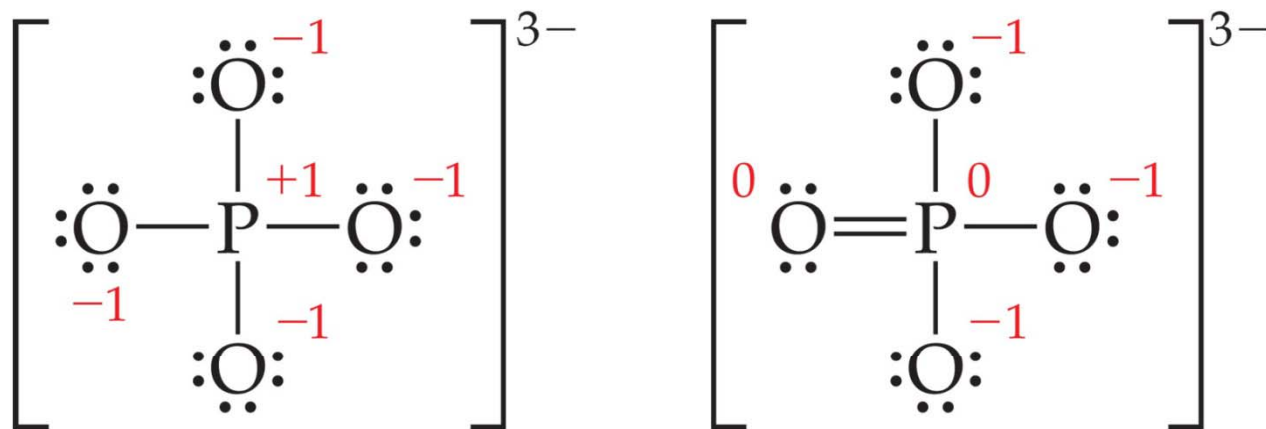
# More Than Eight Electrons



- The only way PCl<sub>5</sub> can exist is if phosphorus has 10 electrons around it.
- It is allowed to expand the octet of atoms on the 3rd row or below.
  - Presumably *d* orbitals in these atoms participate in bonding.

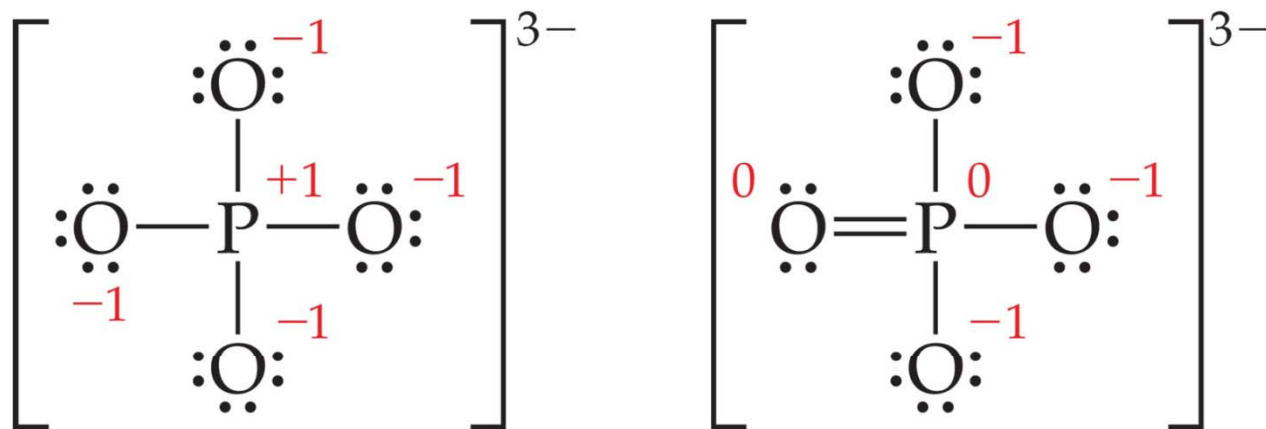
# More Than Eight Electrons

Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, the better structure puts a double bond between the phosphorus and one of the oxygens.



# More Than Eight Electrons

- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is on the 3rd row or below and expanding its octet eliminates some formal charges, do so.



# Covalent Bond Strength



- Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.
- This is the **bond enthalpy**.
- The bond enthalpy for a Cl—Cl bond,  $D(\text{Cl—Cl})$ , is measured to be 242 kJ/mol.



# Average Bond Enthalpies

- This table lists the average bond enthalpies for many different types of bonds.
- Average bond enthalpies are positive, because bond breaking is an endothermic process.

## Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146	Cl—F	253
C—N	293	N—O	201	O—F	190	Cl—Cl	242
C—O	358	N—F	272	O—Cl	203		
C—F	485	N—Cl	200	O—I	234	Br—F	237
C—Cl	328	N—Br	243			Br—Cl	218
C—Br	276			S—H	339	Br—Br	193
C—I	240	H—H	436	S—F	327		
C—S	259	H—F	567	S—Cl	253	I—Cl	208
		H—Cl	431	S—Br	218	I—Br	175
Si—H	323	H—Br	366	S—S	266	I—I	151
Si—Si	226	H—I	299				
Si—C	301						
Si—O	368						
Si—Cl	464						

## Multiple Bonds

C=C	614	N=N	418	O <sub>2</sub>	495
C≡C	839	N≡N	941	S=O	523
C=N	615	N=O	607	S=S	418
C≡N	891				
C=O	799				
C≡O	1072				

# Average Bond Enthalpies

**NOTE:** These are *average* bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH<sub>4</sub>, will be a bit different than the C—H bond in chloroform, CHCl<sub>3</sub>.

## Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
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# Average Bond Enthalpies

## Single Bonds

---

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## Multiple Bonds

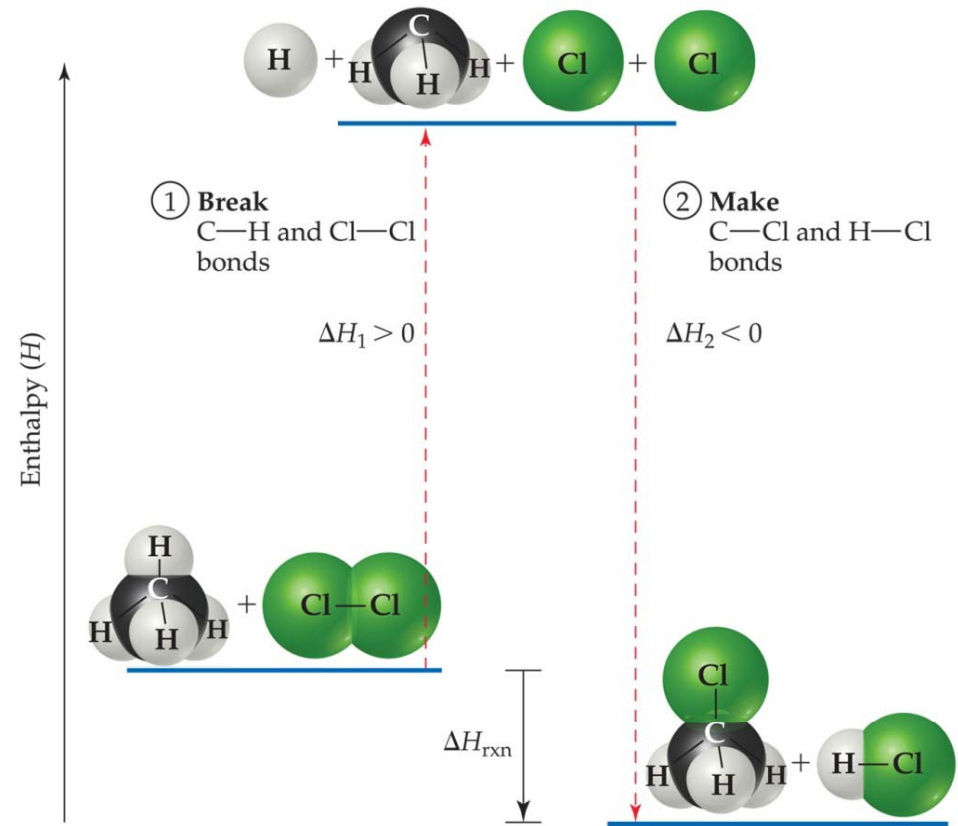
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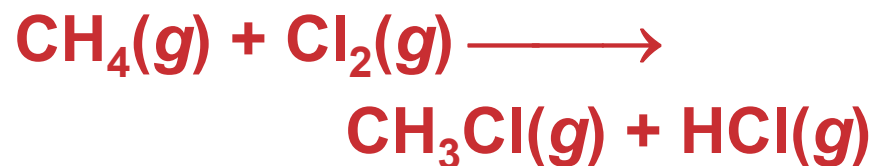
# Enthalpies of Reaction

- Another way to estimate  $\Delta H$  for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.



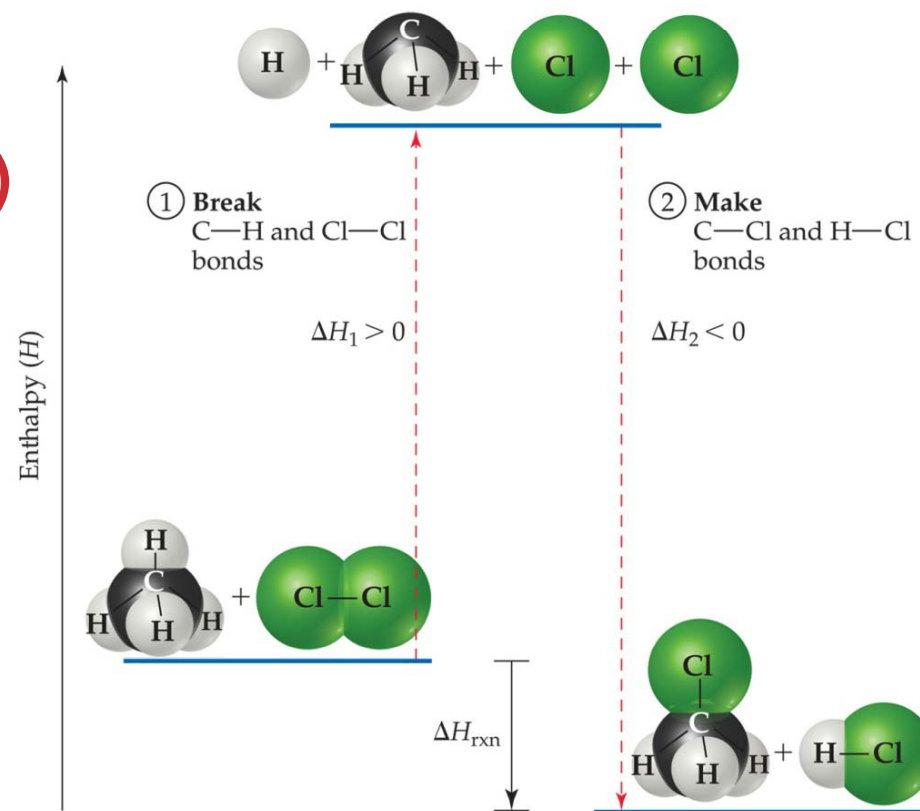
$$\Delta H_{\text{rxn}} = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$

# Enthalpies of Reaction



In this example:

one C—H bond and one Cl—Cl bond are broken;  
one C—Cl and one H—Cl bond are formed.



# Enthalpies of Reaction

So,

$$\begin{aligned}\Delta H_{\text{rxn}} &= [D(\text{C—H}) + D(\text{Cl—Cl}) - [D(\text{C—Cl}) + D(\text{H—Cl})] \\ &= [(413 \text{ kJ}) + (242 \text{ kJ})] - [(328 \text{ kJ}) + (431 \text{ kJ})] \\ &= (655 \text{ kJ}) - (759 \text{ kJ}) \\ &= -104 \text{ kJ}\end{aligned}$$

# Bond Enthalpy and Bond Length

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.