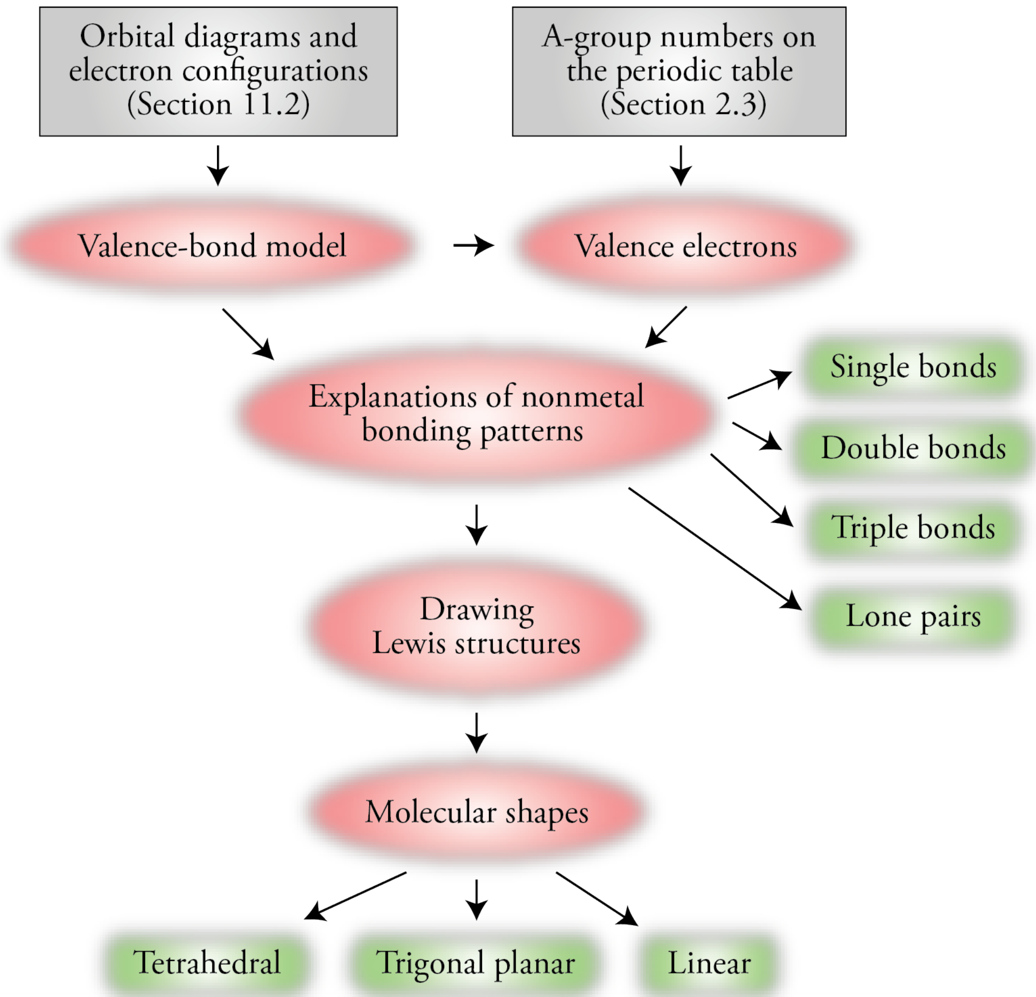
Chapter 12
Molecular Structure

An Introduction to Chemistry

by Mark Bishop

Chapter Map


Orbital diagrams and electron configurations (Section 11.2)
A-group numbers on the periodic table (Section 2.3)
Valence-bond model
Valence electrons
Explanations of nonmetal bonding patterns
Single bonds
Double bonds
Triple bonds
Lone pairs
Drawing Lewis structures
Molecular shapes
Tetrahedral
Trigonal planar
Linear

Models – Advantages and Disadvantages (1)

- They help us to *visualize*, *explain*, and *predict* chemical changes.
- Because a model is a *simplified* version of what we think is true, the processes it depicts are sometimes described using the phrase *as if*. When you read, "It is as if an electron were promoted from one orbital to another," the phrase is a reminder that we do not necessarily think this is what really happens. We merely find it useful to talk about the process as if this is the way it happens.

Models – Advantages and Disadvantages (2)

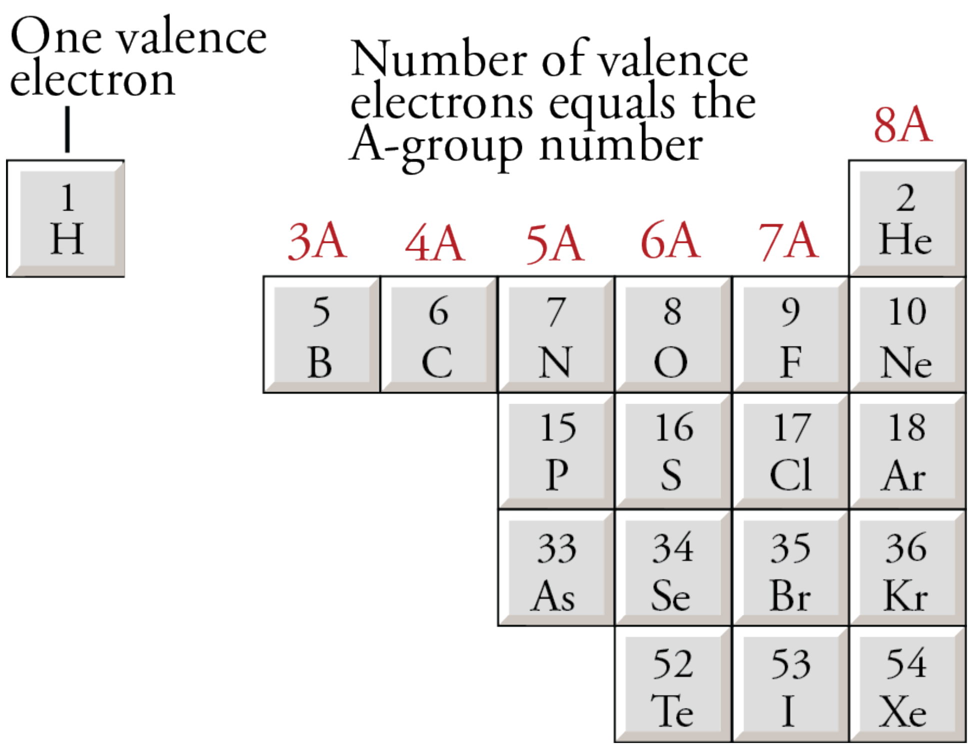
- One characteristic of models is that they ***change with time***. Because our models are simplifications of what we think is real, we are not surprised when they sometimes fail to explain experimental observations. When this happens, the model is altered to fit the new observations.

Assumptions of the Valence-Bond Model

- Only the highest energy electrons participate in bonding.
- Covalent bonds usually form to pair unpaired electrons.

Valence Electrons

- ***Valence electrons*** are the highest-energy *s* and *p* electrons in an atom.



Fluorine

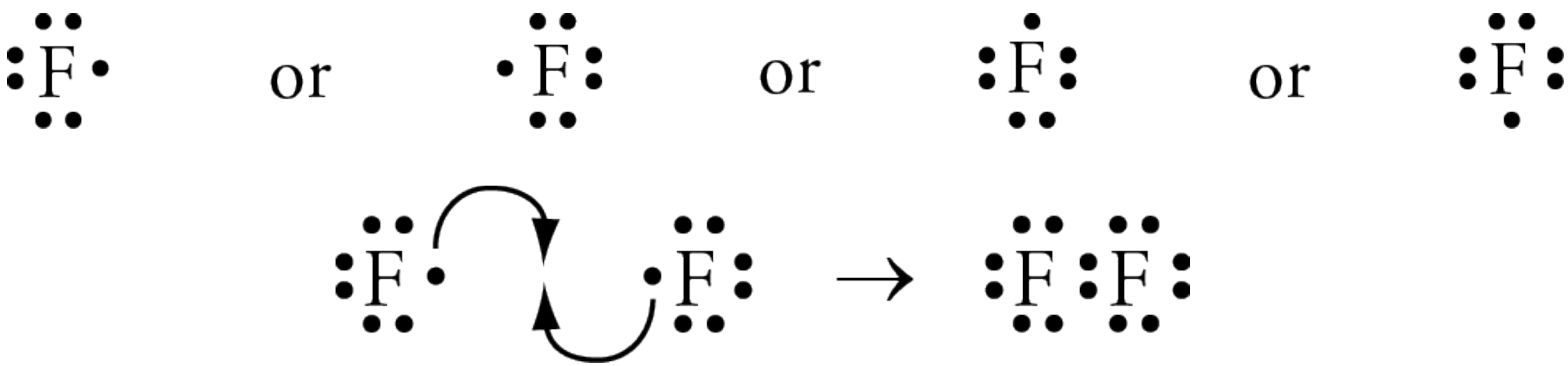
F $1s^2\,2s^2\,2p^5$

$2p$ ↑↓ ↑↓ ↑

$2s$ ↑↓

$1s$ ↑↓

Valence electrons $2s$ ↑↓ $2p$ ↑↓ ↑↓ ↑



H_2 Formation

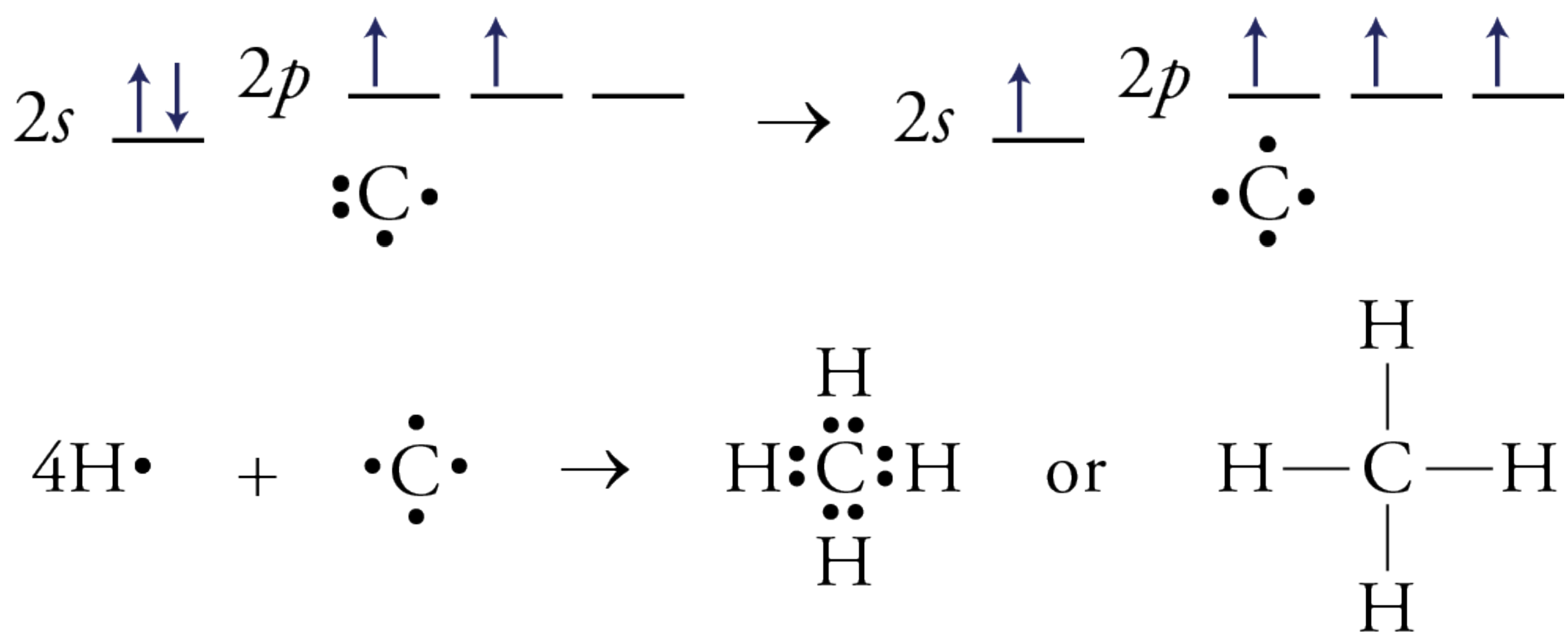
- The unpaired electron on a hydrogen atom makes the atom unstable.

$$\mathrm{H}\bullet \qquad\qquad 1s\ \underline{\ \uparrow\ }$$

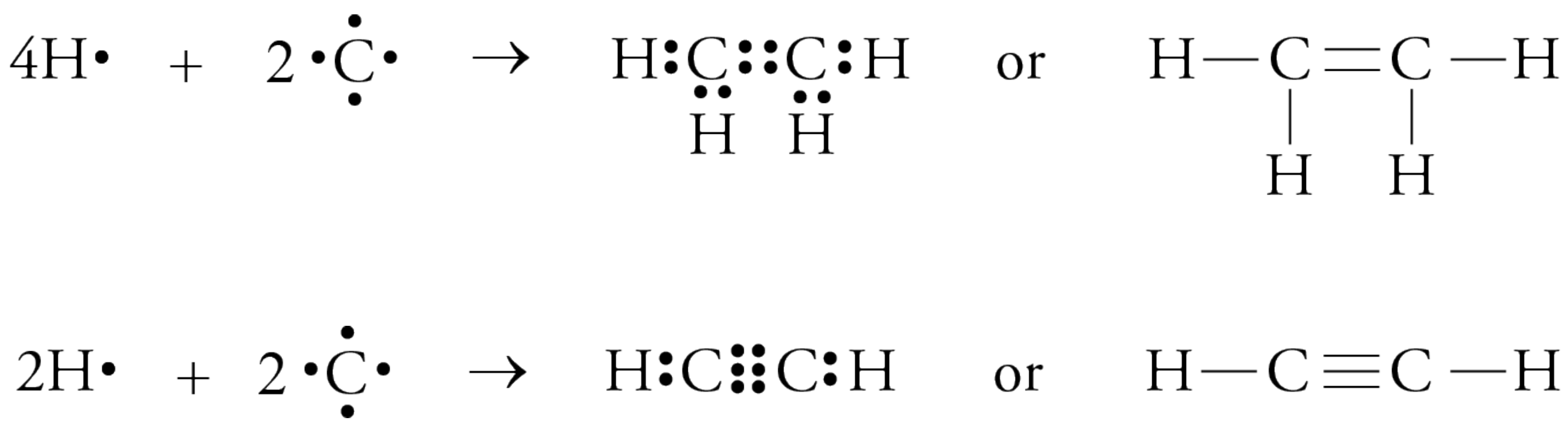
- Two hydrogen atoms combine to form one hydrogen molecule.

$$\mathrm{H}\bullet \quad \bullet\mathrm{H} \rightarrow \mathrm{H}{:}\mathrm{H} \quad \text{or} \quad \mathrm{H}{-}\mathrm{H}$$

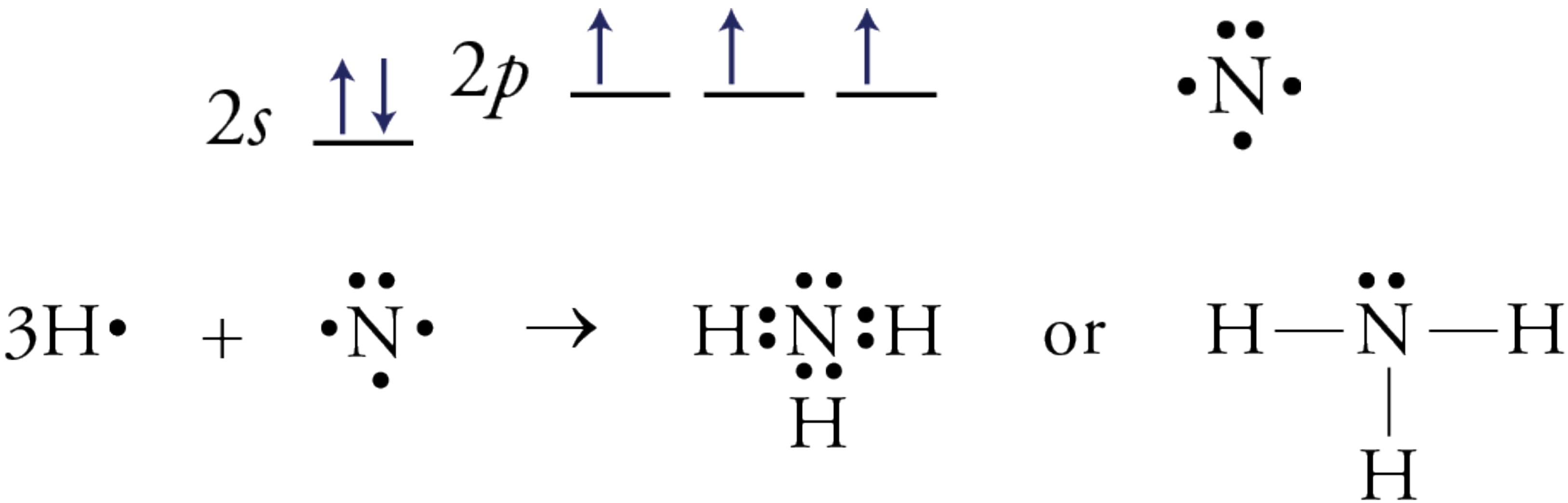
Carbon – 4 bonds



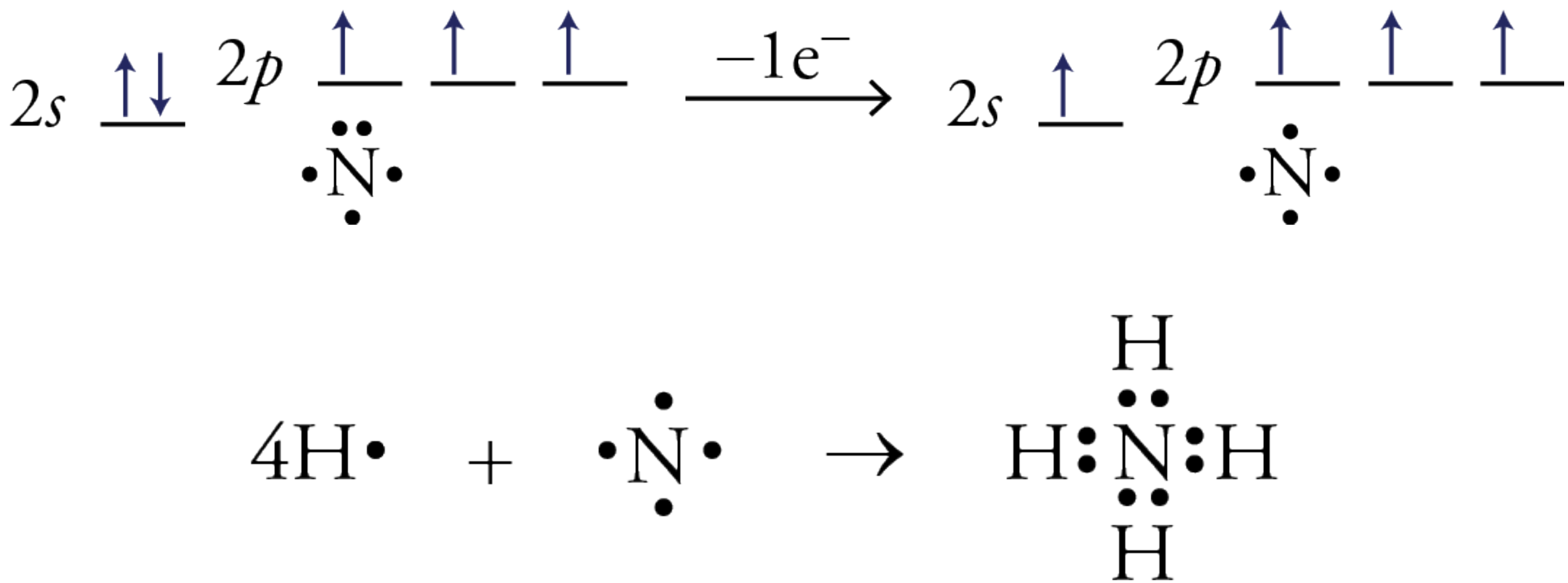
Carbon – Multiple Bonds



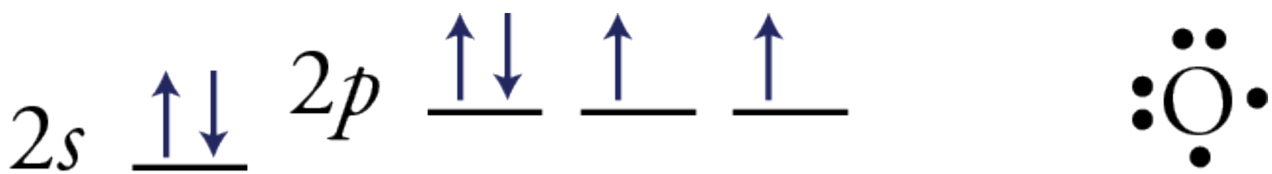
Nitrogen – 3 bonds & 1 lone pair

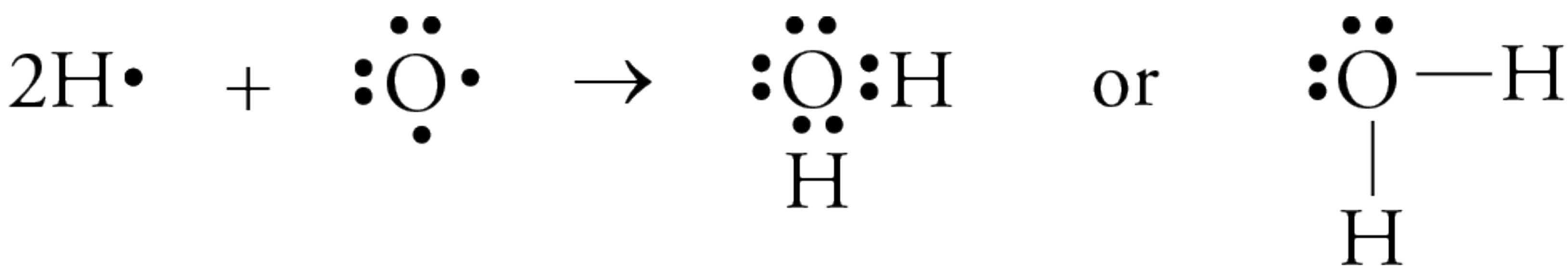


Nitrogen – 4 bonds

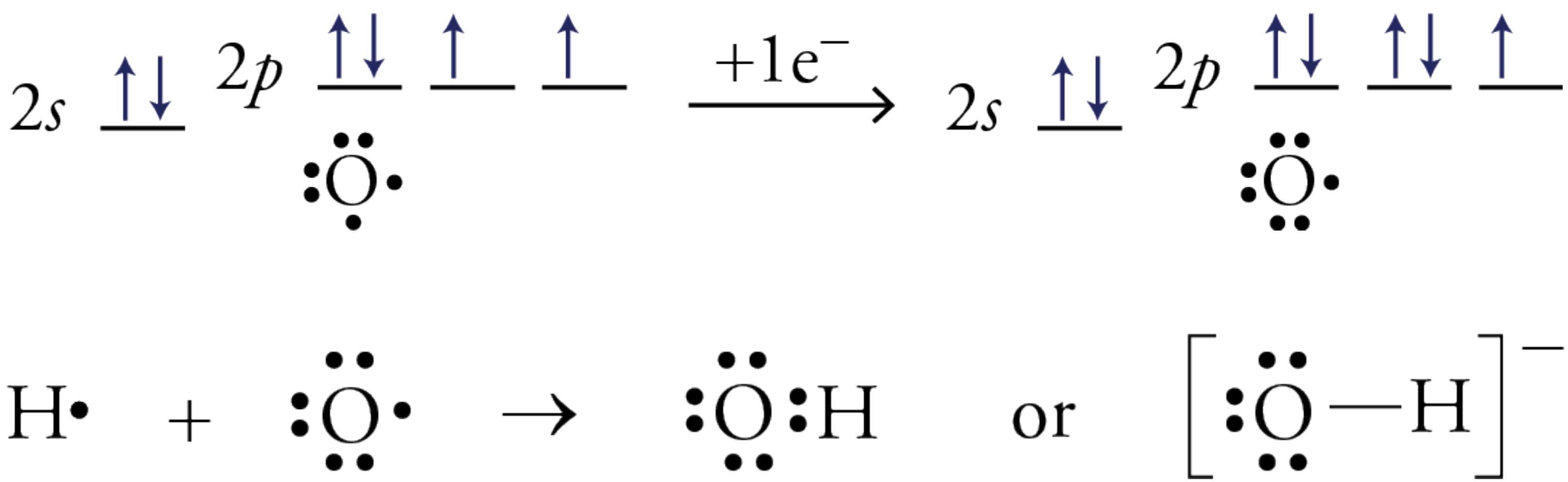


Oxygen – 2 bonds & 2 lone pairs



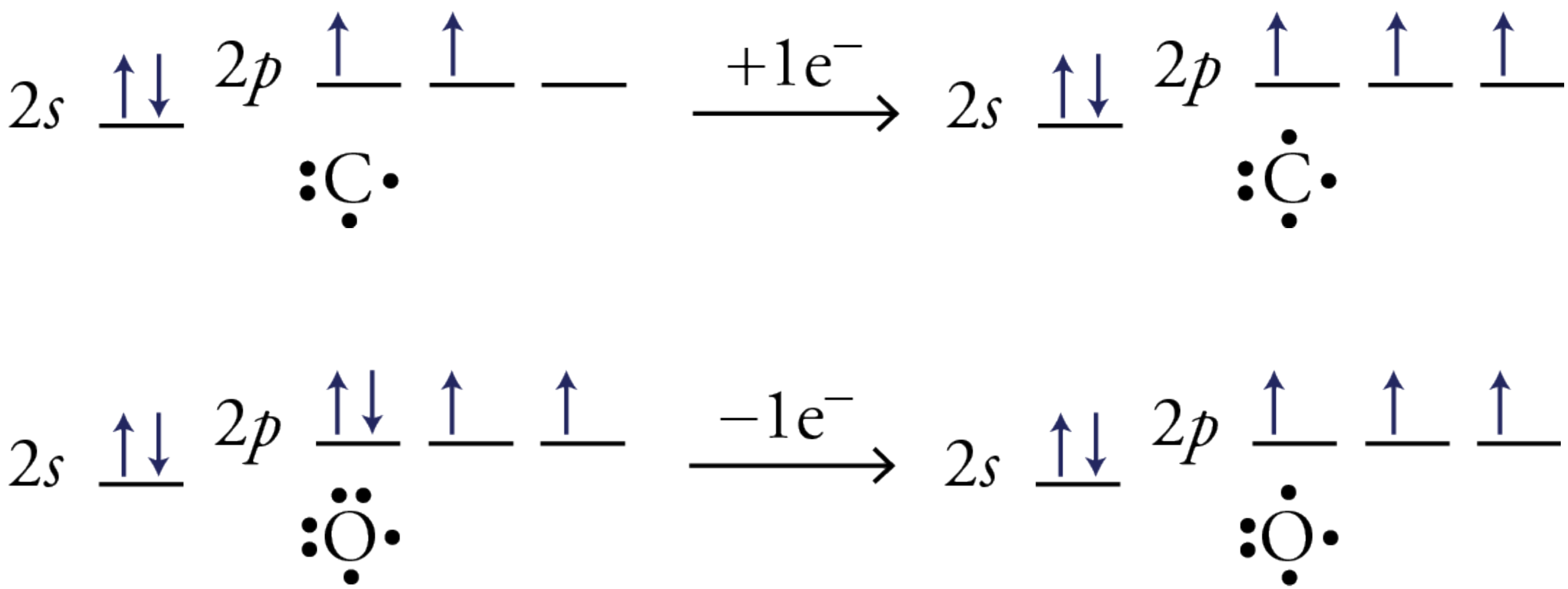


Oxygen – 1 bond & 3 lone pairs

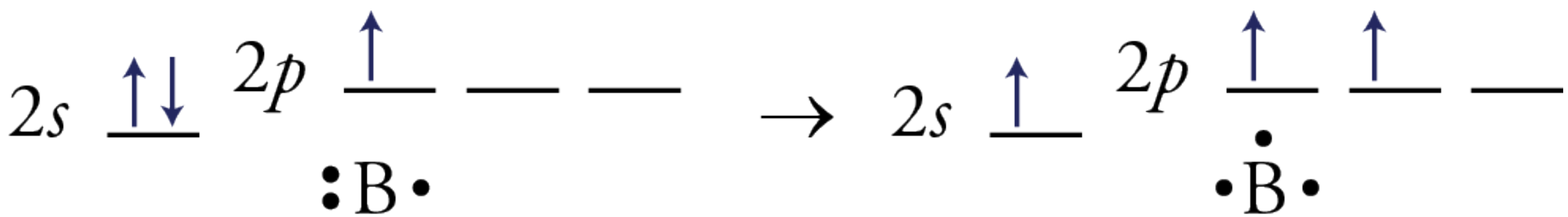


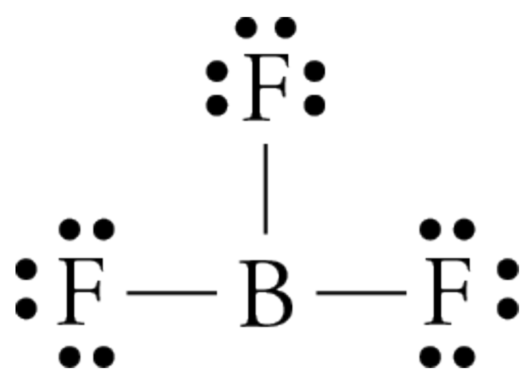
Carbon – 3 bonds & 1 lone pair
Oxygen – 3 bonds & 1 lone pair

$$:C\equiv O:$$



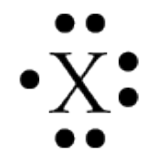
Boron – 3 bonds

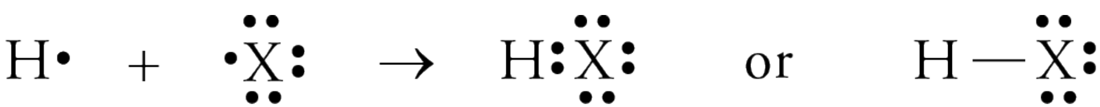




Halogens – 1 bond & 3 lone pairs

$ns\ \underline{\uparrow\downarrow}\ \ np\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\ \ }$





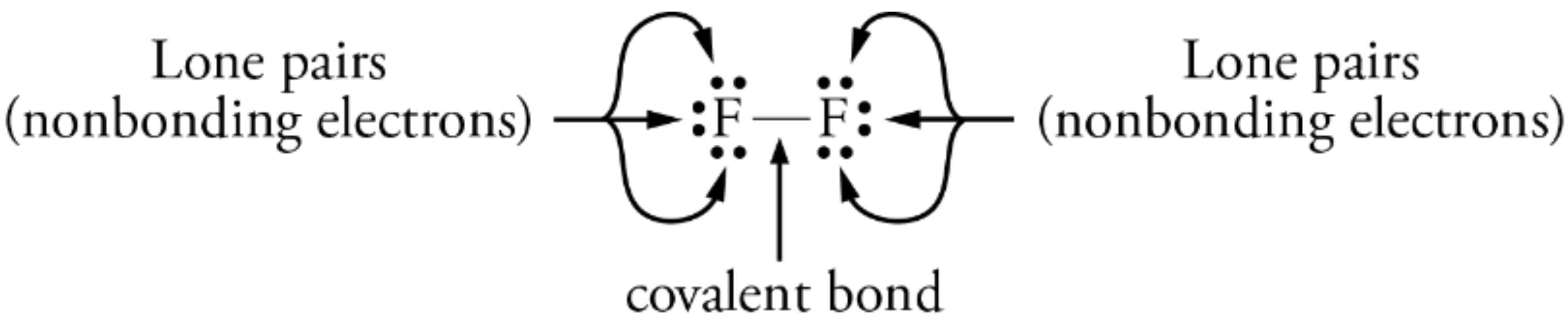
X = F, Cl, Br, or I

Most Common Bonding Patterns for Nonmetals

Element	# Bonds	# lone pairs
H	1	0
C	4	0
N, P	3	1
O, S, Se	2	2
F, Cl, Br, I	1	3

Drawing Lewis Structures

- This chapter describes how to draw Lewis structures from chemical formulas.
- ***Lewis structures*** represent molecules using element symbols, lines for bonds, and dots for lone pairs.



The long way

- Sometimes a Lewis structure cannot be drawn by trying to get the most common bonding pattern.
  - All polyatomic ions have at least one atom that does not have its most common bonding pattern.
  - Although you will not see this in my text, atoms below the second period on the periodic table can have more bonds than are predicted for their most common bonding pattern.

Example 1

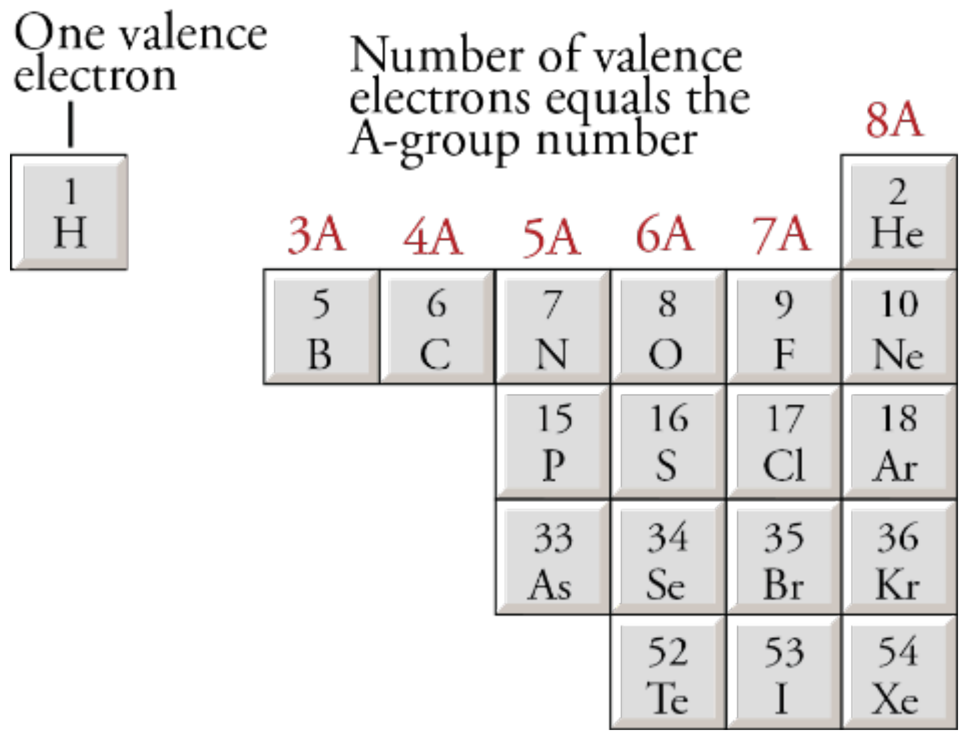
- Example 1: **methyl bromide, CH_3Br**, which is an ozone depleting gas used as a fumigant.

Drawing Lewis Structures (1)

- **Step 1:** Determine the total number of valence electrons for the molecule or polyatomic ion. (These are the electrons that will be represented in your Lewis structure by lines for two-electron bonds and pairs of dots for the lone pairs.)

Valence Electrons

- ***Valence electrons*** are the highest-energy *s* and *p* electrons in an atom.



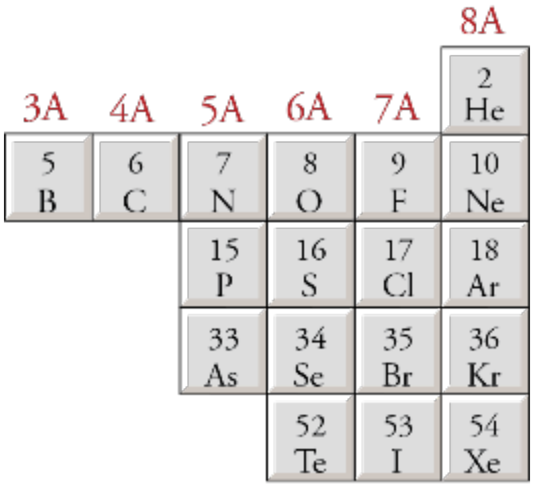
Drawing Lewis Structures (1)

- For uncharged molecules, the total number of valence electrons is the sum of the valence electrons of each atom.
- For polyatomic cations, the total number of valence electrons is the sum of the valence electrons for each atom minus the charge.
- For polyatomic anions, the total number of valence electrons is the sum of the valence electrons for each atom plus the charge.

Example 1
Step 1

Methyl bromide, CH_3Br

- Carbon is in group 4A, so it has four valence electrons.
- Each hydrogen has only one valence electron.
- Bromine is in group 7A, so it has seven valence electrons.
- Total valence electrons $= 4+3(1)+7 = 14$



Drawing Lewis Structures (2)

- **Step 2:** Draw a reasonable skeletal structure, using single bonds to join all the atoms.
  - Try to arrange the atoms to yield the most typical number of bonds for each atom.
  - Apply the following guidelines in deciding what element belongs in the center of your structure.
    - Hydrogen and fluorine atoms are never in the center.
    - Oxygen atoms are rarely in the center.
    - The element with the fewest atoms in the formula is often in the center.
    - The atom that is capable of making the most bonds is often in the center.
  - Oxygen atoms rarely bond to other oxygen atoms.
  - The molecular formula often reflects the molecular structure.
  - Carbon atoms commonly bond to other carbon atoms.

Most Common Bonding Patterns for Nonmetals

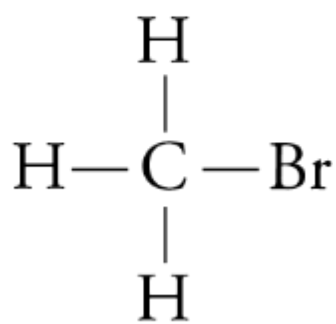
	3A	4A	5A	6A	7A	8A
Number of lone pairs		0	1	2	3	
Number of bonds		4	3	2	1	
						2 He
	5 B	6 C	7 N	8 O	9 F	10 Ne
			15 P	16 S	17 Cl	18 Ar
			33 As	34 Se	35 Br	36 Kr
				52 Te	53 I	54 Xe

https://preparatorychemistry.com/Bishop_periodic_table.pdf

Example 1
Step 2

Methyl bromide, CH_3Br

- Because hydrogen atoms always have one bond, and because bromine usually has only one bond, the H and Br symbols must all be attached to the central carbon.
- Also, because carbon usually forms the most bonds, it is most likely to be in the center.

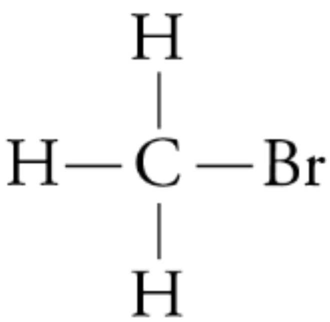


Drawing Lewis Structures (3)

- **Step 3:** Subtract 2 electrons from the total number of valence electrons for each of the single bonds (represented by lines) described in the skeleton from Step 2.

Example 1
Step 3

Methyl bromide, CH_3Br



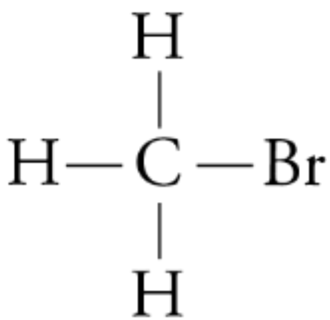
- There are four bonds, so we have used $4 \times 2 = 8$ electrons.
- We have $14 - 8 = 6$ remaining electrons.

Drawing Lewis Structures (4)

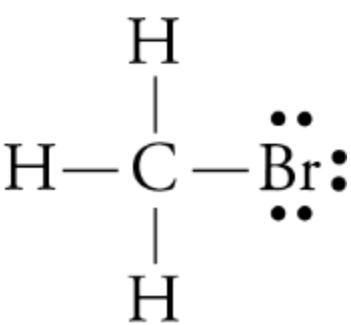
- **Step 4:** Try to distribute the remaining electrons as lone pairs to obtain a total of eight electrons around each atom except hydrogen and boron.
  - In a reasonable Lewis structure, carbon, nitrogen, oxygen, and fluorine always have eight electrons around them.
  - Hydrogen will always have a total of two electrons from its one bond.
  - Boron can have fewer than eight electrons but never more than eight.
  - The nonmetallic elements in periods beyond the second period (P, S, Cl, Se, Br, and I) usually have eight electrons around them, but they can have more.
  - The bonding properties of the metalloids arsenic, As, and tellurium, Te, are similar to those of phosphorus, P, and sulfur, S, so they usually have eight electrons around them but can have more.

Example 1
Step 4

Methyl bromide, CH_3Br



- H never has lone pairs.
- Carbon already has its 4 bonds and an 8 electrons around it, so we add the 6 remaining electron to the Br as 3 lone pairs.

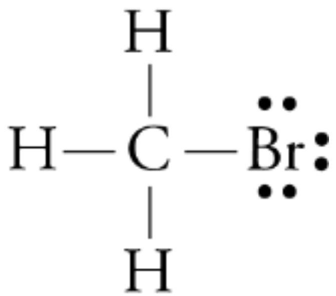


Drawing Lewis Structures (5)

- **Step 5:** Do one of the following.
  - If in Step 4 you were able to obtain an octet of electrons around each atom other than hydrogen and boron, and if you used all of the remaining valence electrons, go to Step 6.
  - If you have electrons remaining after each of the atoms other than hydrogen and boron have their octet, you can put more than eight electrons around elements in periods below the second period. (You will not need to use this procedure for any of the structures in this text, but if you take more advanced chemistry courses, it will be useful.)
  - If you do not have enough electrons to obtain octets of electrons around each atom (other than hydrogen and boron), convert one lone pair into a multiple bond for each two electrons that you are short.

Example 1
Step 5

Methyl bromide, CH_3Br



- The four bonds to the carbon atom give it an octet around it ($4 \times 2 = 8$).
- The hydrogen atoms have their one bond.
- The one bond and three lone pairs for the bromine atom give it an octet around it.

Drawing Lewis Structures (6 & 7)

- **Step 6:** Check your structure to see if all of the atoms have their most common bonding pattern.
- **Step 7:** If necessary, try to rearrange your structure to give each atom its most common bonding pattern. One way to do this is to return to Step 2 and try another skeleton. (This step is unnecessary if all of the atoms in your structure have their most common bonding pattern.)

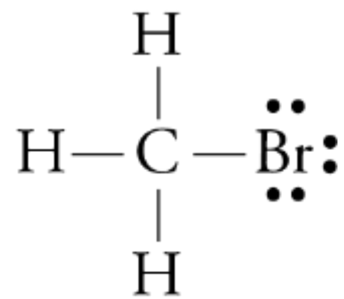
Most Common Bonding Patterns for Nonmetals

	3A	4A	5A	6A	7A	8A
Number of lone pairs		0	1	2	3	
Number of bonds		4	3	2	1	
						2 He
	5 B	6 C	7 N	8 O	9 F	10 Ne
			15 P	16 S	17 Cl	18 Ar
			33 As	34 Se	35 Br	36 Kr
				52 Te	53 I	54 Xe

https://preparatorychemistry.com/Bishop_periodic_table.pdf

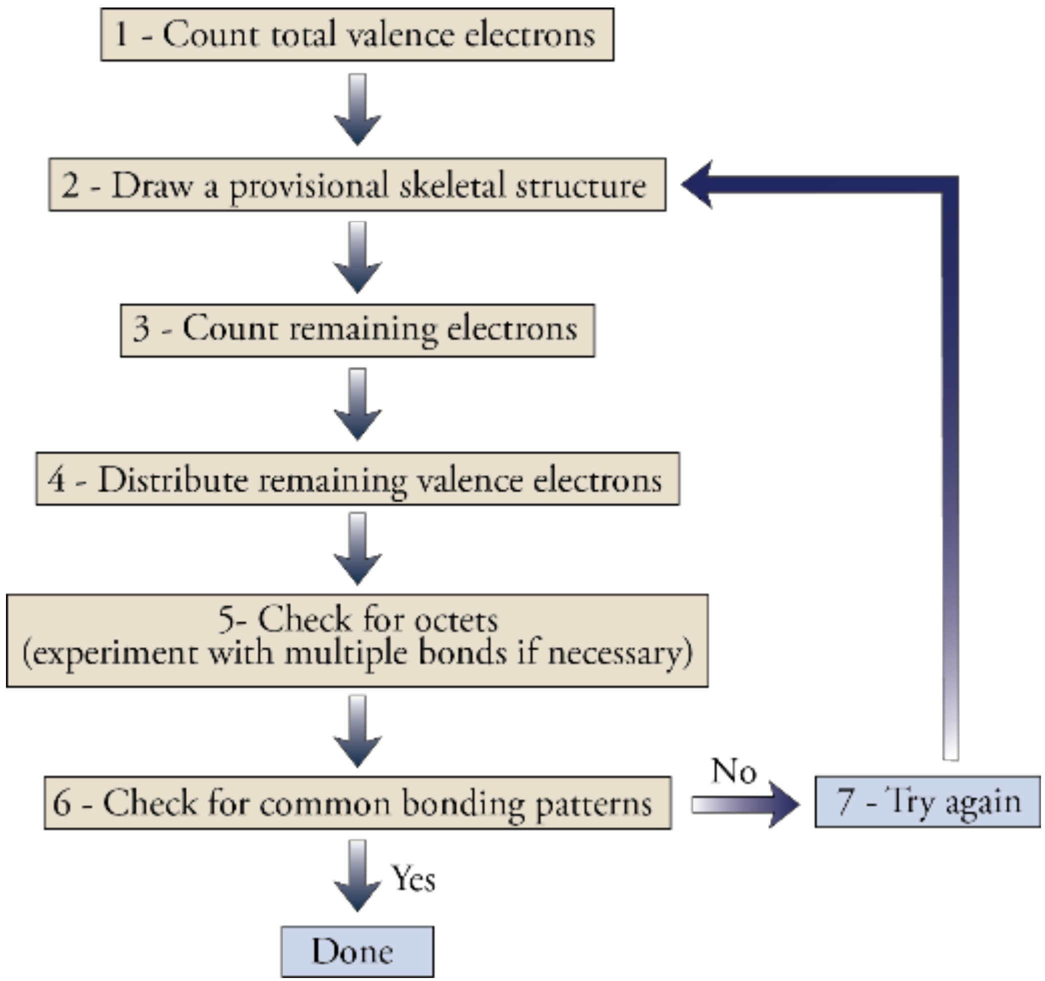
Example 1
Steps 6 and 7

Methyl bromide, CH_3Br



- All of the atoms have their most common bonding pattern, so step 7 is unnecessary.

Lewis Structure Drawing Summary



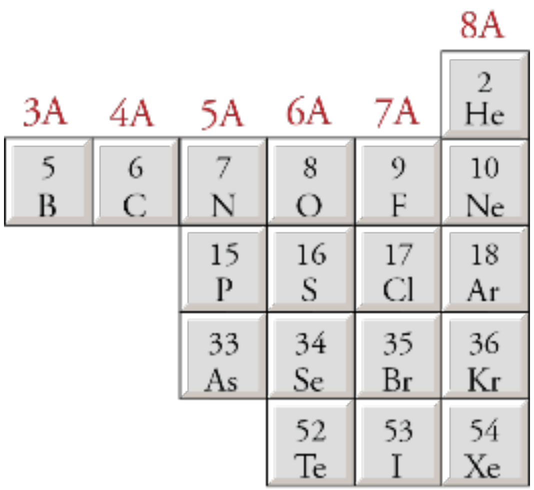
Example 2

- **Formaldehyde, CH_2O**, has many uses, including the preservation of biological specimens.

Example 2
Step 1

Formaldehyde, CH_2O

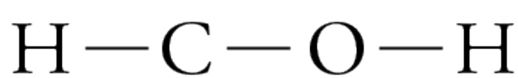
- Each hydrogen has one valence electron.
- Carbon is in group 4A, so it has four valence electrons.
- Oxygen is in group 6A, so it has six valence electrons.
- Total valence electrons
  $= 4+2(1)+6 = 12$

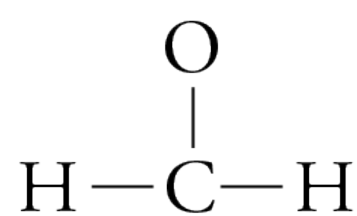


Example 2
Step 2

Formaldehyde, CH_2O

- Hydrogen atoms always have one bond, oxygen atoms usually have two bonds and carbon atoms usually have four bonds.
- There are two possible skeletons at this point.





Example 2
Step 3

Formaldehyde, CH_2O

H—C—O—H

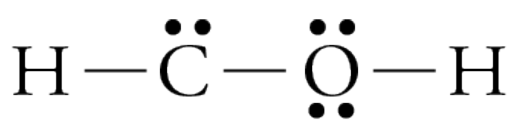
- There are three bonds, so we have used $3 \times 2 = 6$ electrons.
- We have $12 - 6 = 6$ remaining electrons.

Example 2
Step 4

Formaldehyde, CH_2O

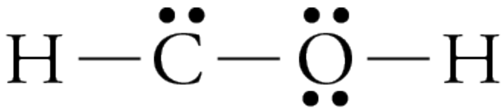
H—C—O—H

- H never has lone pairs.
- We know that oxygen atoms' most common bonding pattern is 2 bonds and 2 lone pairs, so we put 2 lone pairs on the O.
- We only have 2 of our 6 valence electrons remaining, so we put the last 2 electrons on the C.

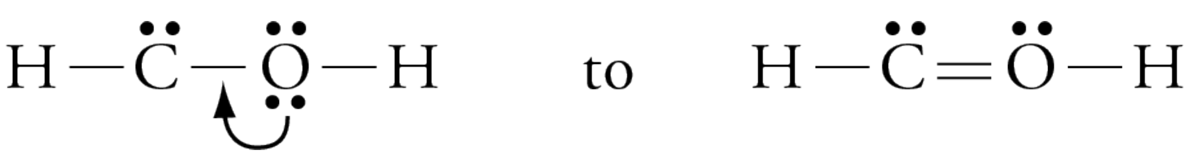


Example 2
Step 5

Formaldehyde, CH_2O

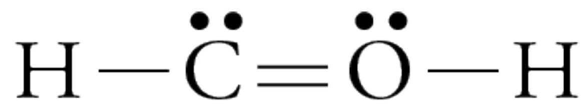


- If you do not have enough electrons to obtain octets of electrons around each atom (other than hydrogen and boron), convert one lone pair into a multiple bond for each two electrons that you are short.
- We need to get 2 more electrons around the C and keep 8 electrons around the O, so we shift one of the lone pairs on O to form another bond to C.

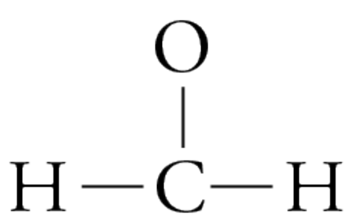


Example 2
Steps 6 and 7

Formaldehyde, CH_2O



- Neither carbon nor oxygen have their most common bonding pattern, so we need to go back to Step 2 and try a different skeleton in hopes of getting the most common bonding patterns.



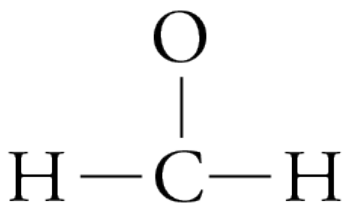
Example 2
Step 1

Formaldehyde, CH_2O

- Carbon is in group 4A, so it has four valence electrons.
- Each hydrogen has one valence electron.
- Oxygen is in group 6A, so it has six valence electrons.
- Total valence electrons = 4+2(1)+6 = 12

Example 2
Step 3

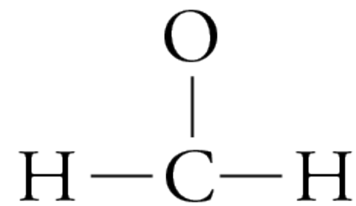
Formaldehyde, CH_2O



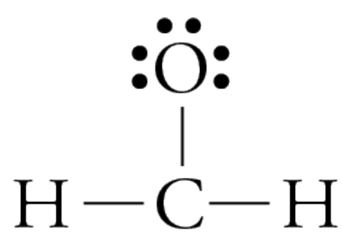
- There are three bonds, so we have used $3 \times 2 = 6$ electrons.
- We have $12 - 6 = 6$ remaining electrons.

Example 2
Step 4

Formaldehyde, CH_2O



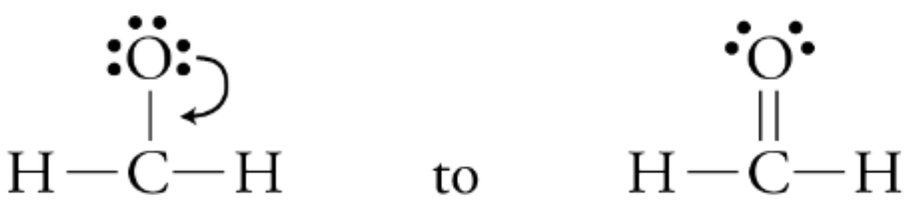
- H never has lone pairs.
- We know that oxygen atoms commonly have lone pairs and carbon atoms rarely do, so use our remaining 6 electrons to put 3 lone pairs on the O.



Example 2
Step 5

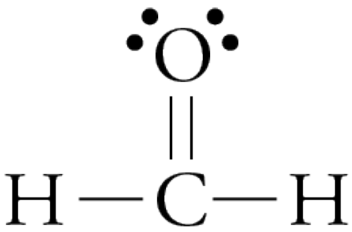
Formaldehyde, CH_2O

- If you do not have enough electrons to obtain octets of electrons around each atom (other than hydrogen and boron), convert one lone pair into a multiple bond for each 2 electrons that you are short.
- We need to get 2 more electrons around the C and keep 8 electrons around the O, so we shift one of the lone pairs on O to form another bond to C.



Example 2
Steps 6 and 7

Formaldehyde, CH_2O



- All of the atoms have their most common bonding pattern, so we have a reasonable Lewis structure.

Example 3

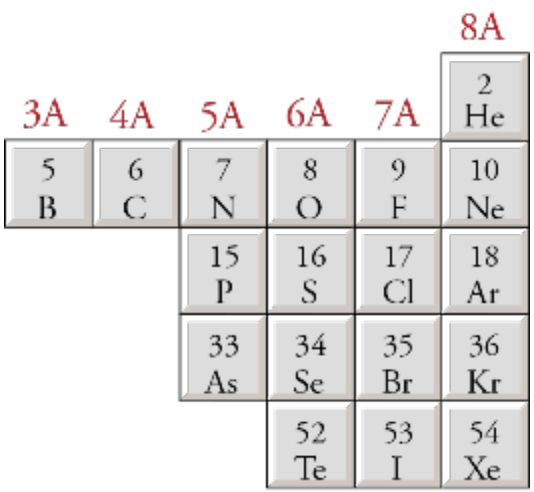
- The **cyanide polyatomic ion, CN^-** is similar in structure to carbon monoxide, CO. Although they work by different mechanisms, they are both poisons that can disrupt the use of oxygen, O_2, in organisms.

Example 3
Step 1

Cyanide, CN^{-}

- Carbon is in group 4A, so it has four valence electrons.
- Nitrogen is in group 5A, so it has five valence electrons.
- We add one more electron for the negative charge.
- Total valence electrons

  = 4+5+1 = 10



Example 3
Step 2

Cyanide, CN^-

- There is only one option for the skeleton. We connect the C to the N.

$$\mathrm{C}-\mathrm{N}$$

Example 3
Step 3

Cyanide, CN^-

$$C - N$$

- There is one bond, so we have used 2 electrons.
- We have 10 – 2 = 8 remaining electrons.

Example 3
Step 4

Cyanide, CN^-

$$\text{C} - \text{N}$$

- We could distribute the remaining 8 electrons in different ways, but let's put two lone pairs on each atom.

$$:\ddot{\text{C}} - \ddot{\text{N}}:$$

Example 3
Step 5

Cyanide, CN^-

- There are only 6 electrons around both C and N, and both have 8 around them in a good Lewis structure, so we need to convert two lone pairs into bonds.
- We shift one lone pair from C and one lone pair from N to form two more bonds between them.
- We put polyatomic ions in brackets for their Lewis structures, and we put the charge as a superscript outside the brackets.

Example 3
Steps 6 and 7

Cyanide, CN^-

$$[:C \equiv N:]^-$$

- The carbon atom does not have its most common bonding pattern, but there is no other option for a skeleton.
- There is always at least one atom in a polyatomic ion that has a bonding pattern other than the most common bonding pattern.

Example 4

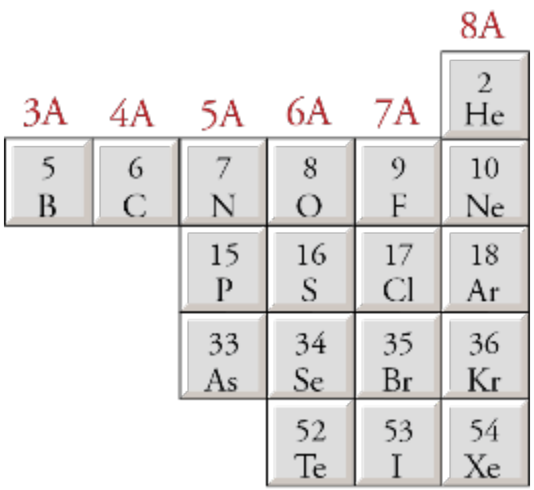
- **CF_3CHCl_2**, the molecular formula for HCFC-123, which is one of the hydrochlorofluorocarbons used as a less damaging replacement for chlorofluorocarbons, which destroy ozone in the stratosphere.

Example 4
Step 1

HCFC-123, CF_3CHCl_2

- Carbon is in group 4A, so it has 4 valence electrons.
- Fluorine and chlorine are in group 7A, so they have 7 valence electrons.
- Hydrogen has 1 valence electron.
- Total valence electrons

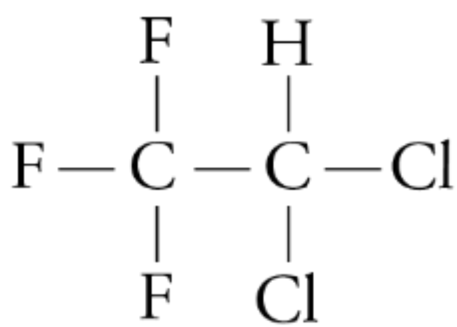
$$= 2(4)+3(7)+1+2(7) = 44$$



Example 4
Step 2

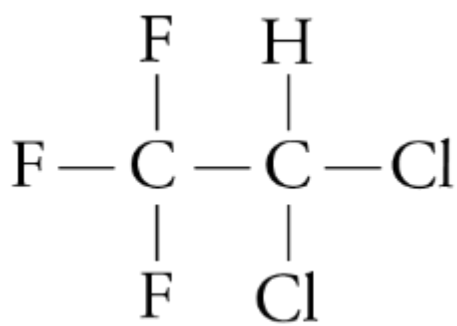
HCFC-123, CF_3CHCl_2

- The formula tells us that there are 3 F atoms on one C and that the H and the 2 Cl atoms must be attached to the other C.
- We'll see more clearly in a later session on molecular geometry that it does not make any difference how you arrange the 2 Cl atoms and the H on the right C.



Example 4
Step 3

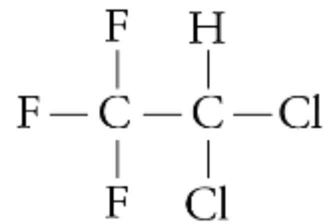
HCFC-123, CF_3CHCl_2



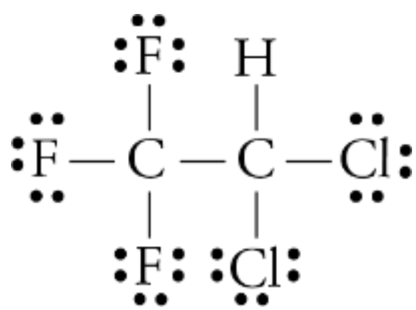
- There are 7 bonds, so we have used $7 \times 2 = 14$ electrons.
- We have 44 – 14 = 30 remaining electrons.

Example 4
Step 4

HCFC-123, CF_3CHCl_2



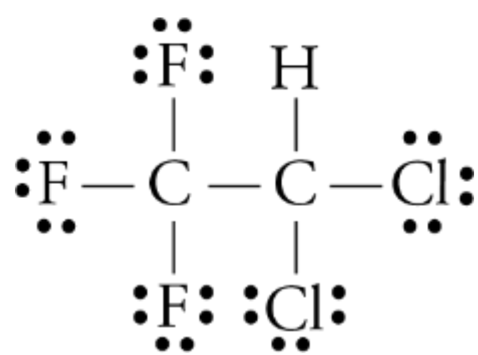
- The C atoms have 8 electrons around them, and the H has its one bond.
- F atoms always have 8 electrons around them, and Cl atoms usually do, so we use all of our remaining 30 electrons to put three lone pairs on all of the F and Cl atoms.



Example 4
Step 5

HCFC-123, CF_3CHCl_2

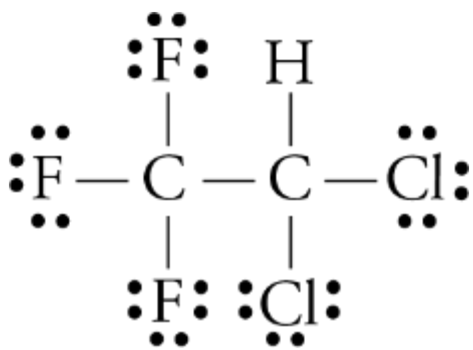
- All of the atoms except hydrogen have their octets of electrons, so we can move on to steps 6 and 7.



Example 4
Steps 6 and 7

HCFC-123, CF_3CHCl_2

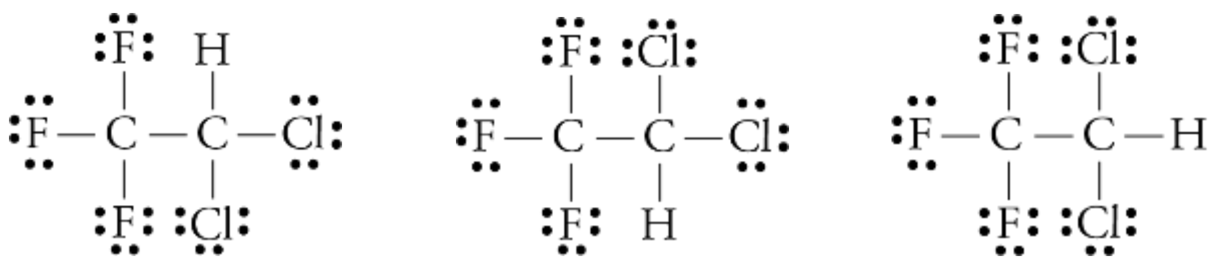
- Every atom has its most common bonding pattern, so we have a good Lewis structure.



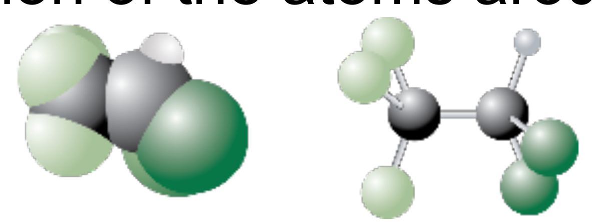
Example 4
Steps 6 and 7

HCFC-123, CF_3CHCl_2

- It might seem like there could be three different Lewis structures for this, but the examples below all describe the same thing.



- The models below might help you to see why. There is rotation of the atoms around the C-C bond.



Example 5

- Acetaldehyde can be converted into the sedative chloral hydrate (the "Mickey Finn" or knockout drops often mentioned in detective stories). In the first step of the reaction that forms chloral hydrate, acetaldehyde, **CH_3CHO**, changes to its isomer, **CH_2CHOH**.

Example 5
Step 1

Acetaldehyde, CH_3CHO

- Carbon is in group 4A, so each C has 4 valence electrons.
- Oxygen is in group 6A, so it has 6 valence electrons.
- Hydrogen has 1 valence electron.
- Total valence electrons

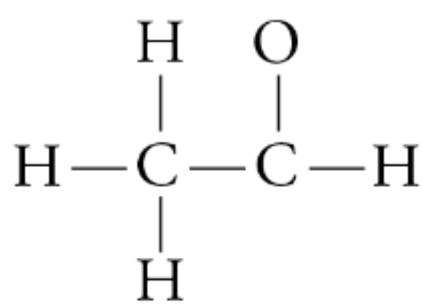
$$= 2(4)+4(1)+6 = 18$$

3A	4A	5A	6A	7A	8A
					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
		15 P	16 S	17 Cl	18 Ar
		33 As	34 Se	35 Br	36 Kr
			52 Te	53 I	54 Xe

Example 5
Step 2

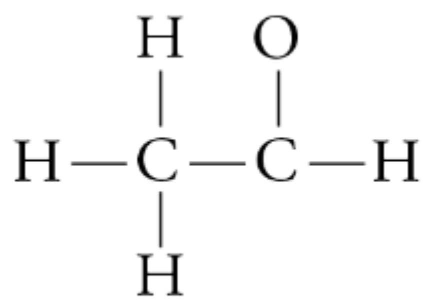
Acetaldehyde, CH_3CHO

- The formula tells us that there are 3 H atoms on one C and that the H and O are on the other C.
- We know that carbon almost always has 4 bonds, so putting both the H and the O on the right C gets us closer to this.



Example 5
Step 3

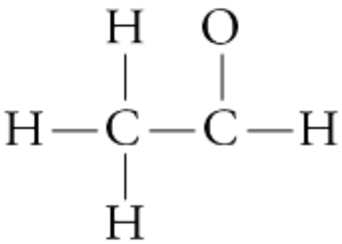
Acetaldehyde, CH_3CHO



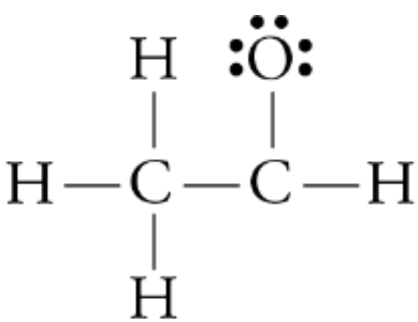
- There are 6 bonds, so we have used $6 \times 2 = 12$ valence electrons.
- We have $18 - 12 = 6$ remaining electrons.

Example 5
Step 4

Acetaldehyde, CH_3CHO



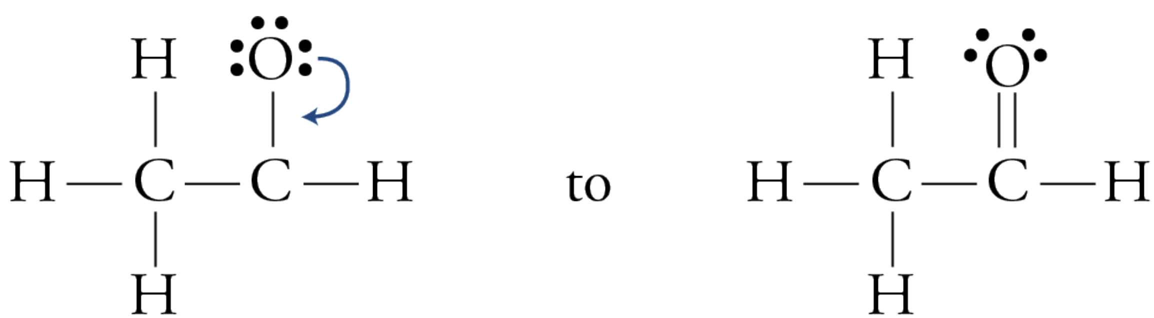
- The left C atom has 8 electrons around it, and the H atoms each have one bond.
- Because C rarely has lone pairs, we put our remaining 6 electrons on the O as lone pairs.



Example 5
Step 5

Acetaldehyde, CH_3CHO

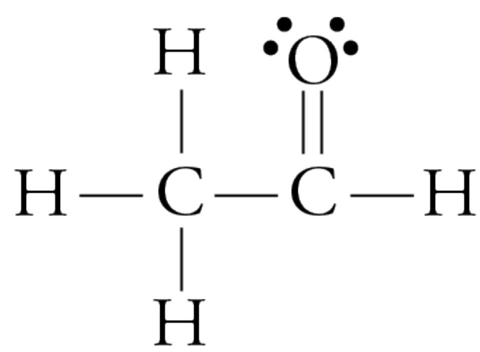
- The right C is short two electrons for its octet, so we move one lone pair from the O to form a second bond between the C and O.



Example 5
Steps 6 and 7

Acetaldehyde, CH_3CHO

- Every atom has it most common bonding pattern, so we have a good Lewis structure.

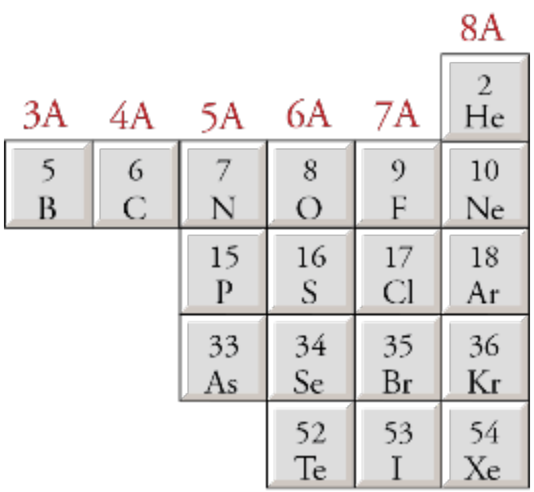


Example 5
Step 1

CH_2CHOH

- Carbon is in group 4A, so each C has 4 valence electrons.
- Oxygen is in group 6A, so it has 6 valence electrons.
- Hydrogen has 1 valence electron.
- Total valence electrons

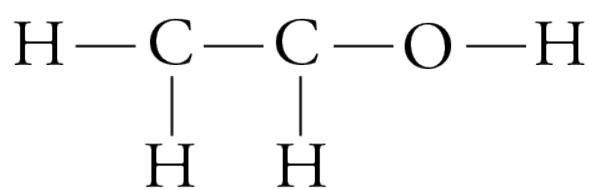
$$= 2(4)+4(1)+6 = 18$$



Example 5
Step 2

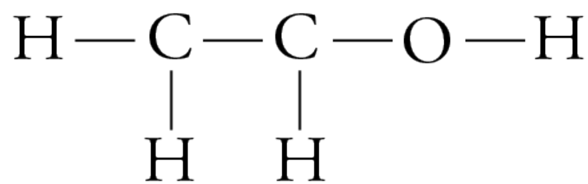
CH_2CHOH

- The formula tells us that there are 2 H atoms on the left C.
- Because one of the remaining H atoms is next to the right C and the other is next to the O, we can assume that the following skeleton is most likely.



Example 5
Step 3

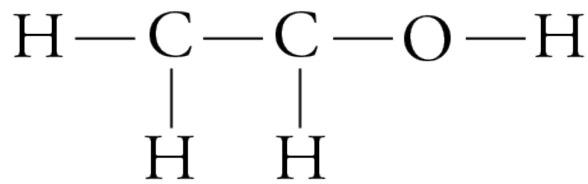
CH_2CHOH



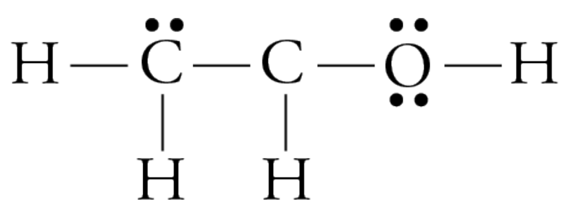
- There are 6 bonds, so we have used $6 \times 2 = 12$ valence electrons.
- We have 18 – 12 = 6 remaining electrons.

Example 5
Step 4

CH_2CHOH

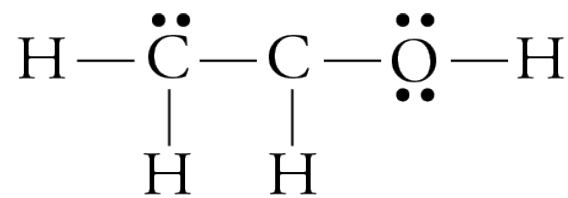


- The H atoms each have one bond.
- Because we know that O atoms are more likely to have lone pairs, we add two lone pairs to the O to give it its octet. The remaining two electrons can go on either C.

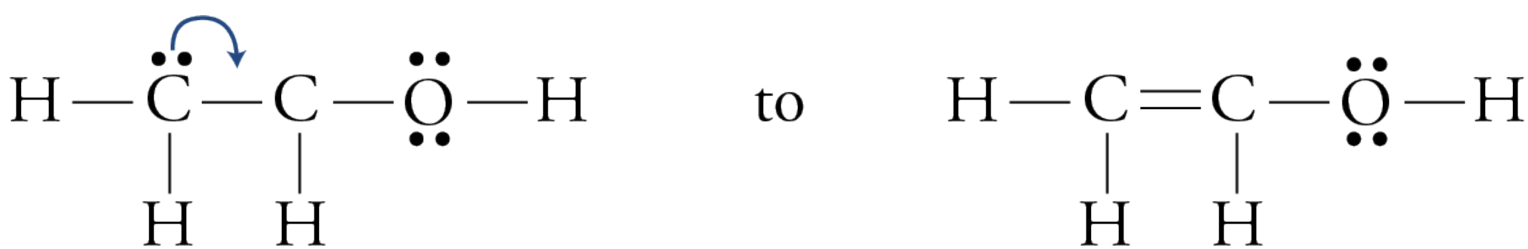


Example 5
Step 5

CH_2CHOH



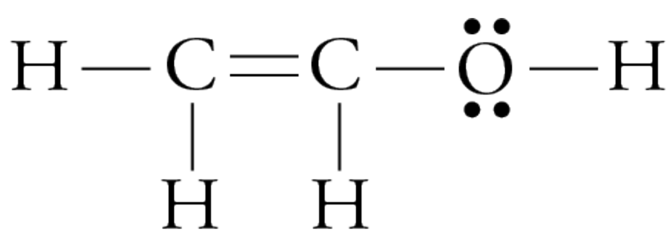
- The right C is short two electrons for its octet, so we move one lone pair from the left C to form a second bond between the C atoms.



Example 5
Steps 6 and 7

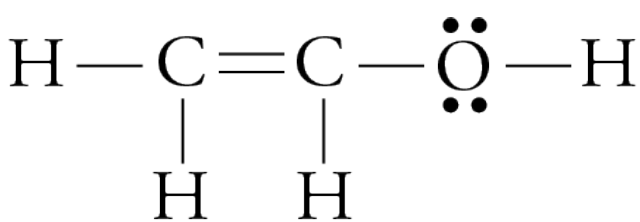
CH_2CHOH

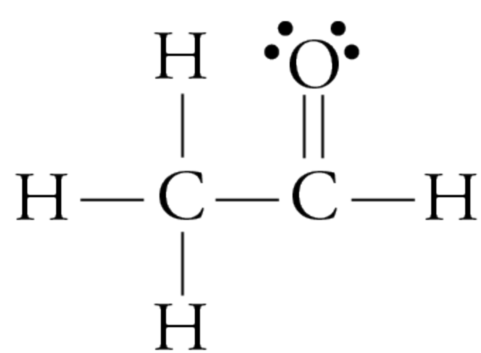
- Every atom has it most common bonding pattern, so we have a good Lewis structure.



Isomers

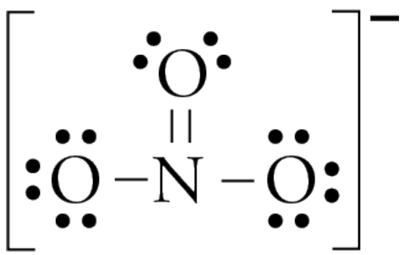
- CH_3CHO and CH_2CHOH are isomers.
- **Isomers** are molecules that have the same atoms (or the same molecular formula, in this case C_2H_4O) but a different arrangement of the atoms (or a different structure, in this case the structures you see below).





Nitrate, NO_3^-

- Lewis structure for nitrate, NO_3^-



- Seems to indicate that the N=O bond is different from the other two N-O bonds.
- Double bonds are shorter and stronger than single bonds.
- All three bonds are the same strength and length, so we need a new component for our Lewis structure process to explain this.

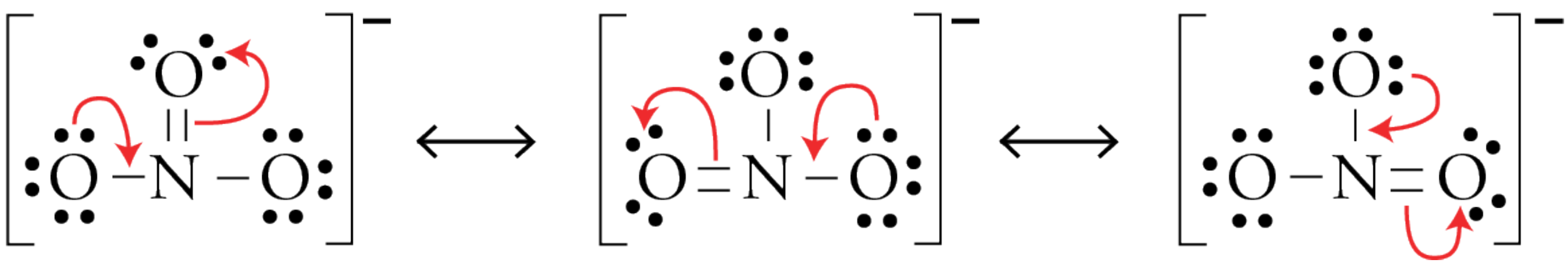
Resonance

- We can view certain molecules and polyatomic ions as if they were able to switch back and forth or resonate between two or more different structures. Each of these structures is called a ***resonance structure***. The switching from one resonance structure to another is called ***resonance***.
- We don't think this is really happening, but as we will see, we think it is useful to think of it *as if* it was happening.

Nitrate Resonance

It is as if this lone pair forms a second bond...

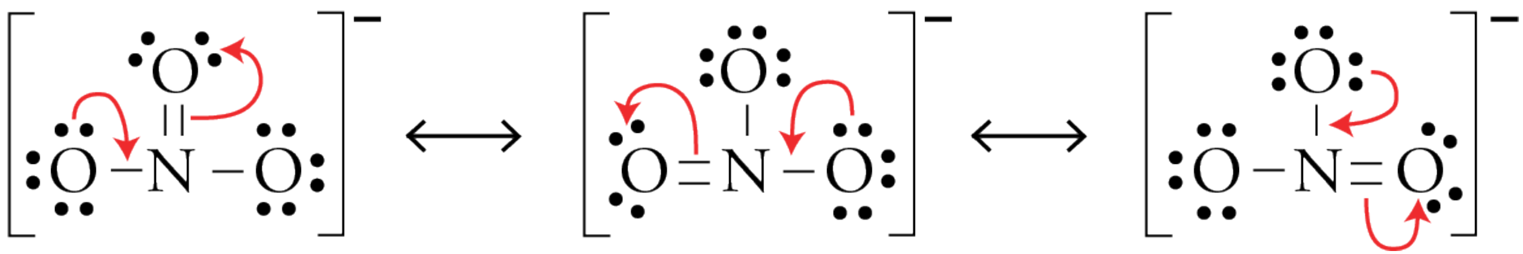
...pushing the electrons in this bond off to form a lone pair.

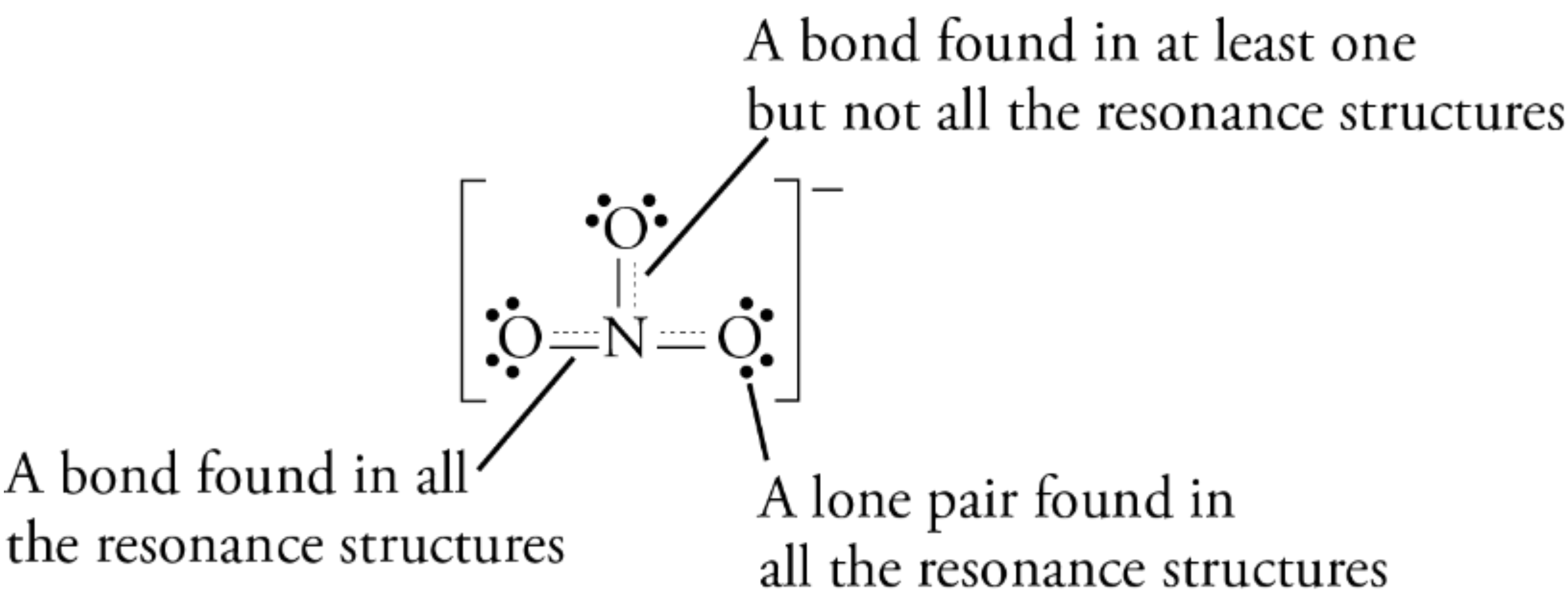


Resonance Hybrid

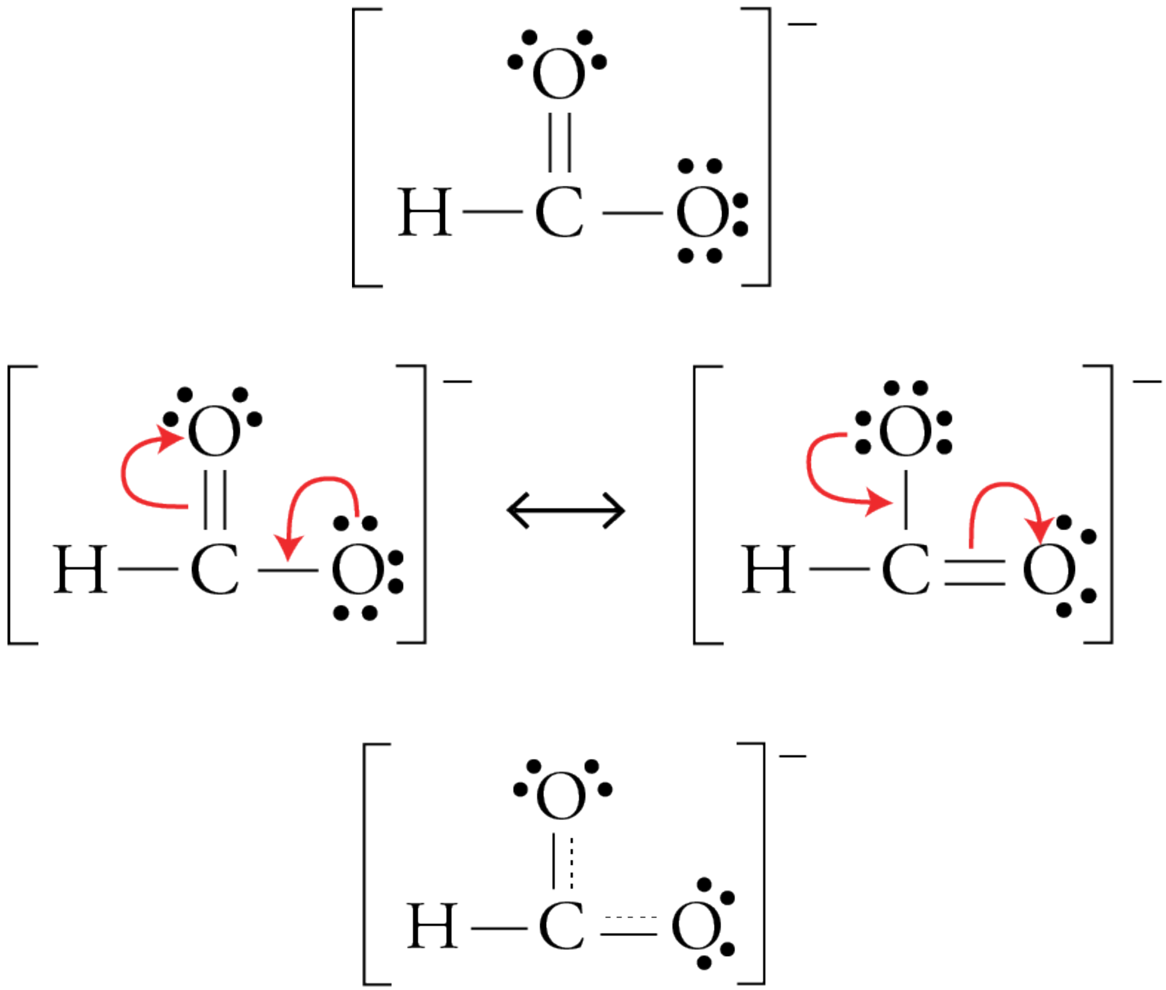
- To blend the resonance structures into a single resonance hybrid:
  - Step 1: Draw the skeletal structure, using solid lines for the bonds that are found in all of the resonance structures.
  - Step 2: Where there is sometimes a bond and sometimes not, draw a dotted line.
  - Step 3: Draw only those lone pairs that are found on every one of the resonance structures. (Leave off the lone pairs that are on one or more resonance structure but not on all of them.)

Nitrate Resonance

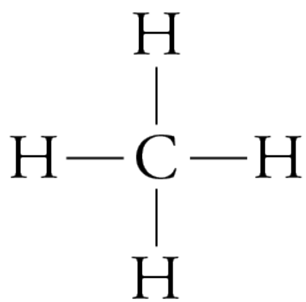


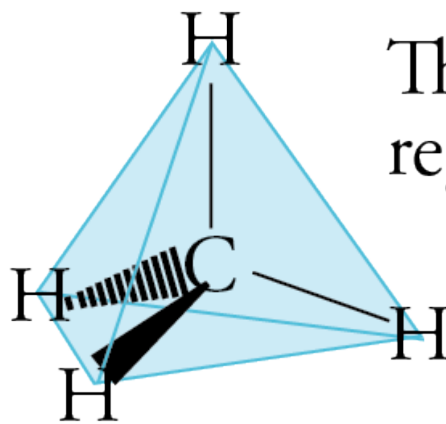


Formate, HCO_2^-

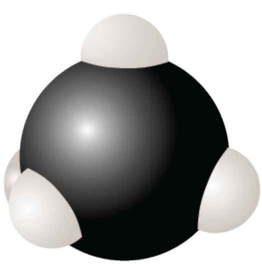


Methane, CH_4

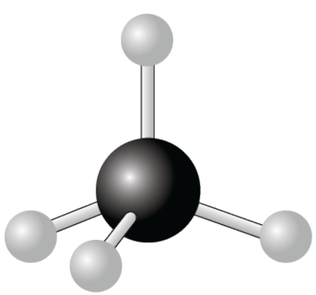




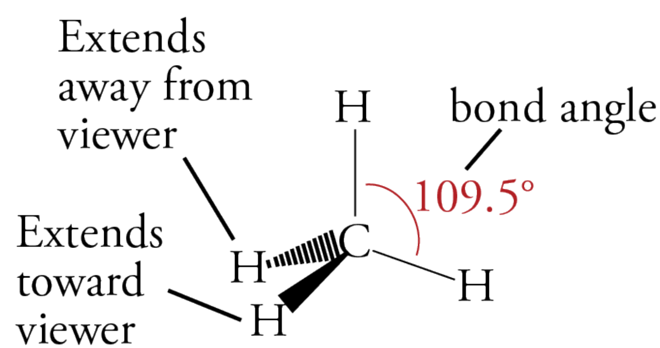
The shaded shape is a regular tetrahedron.



Space-filling model

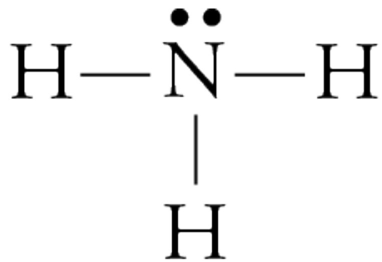


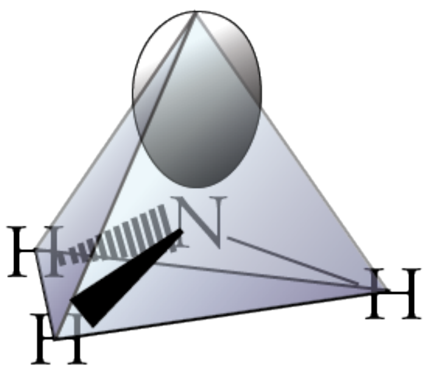
Ball-and-stick model



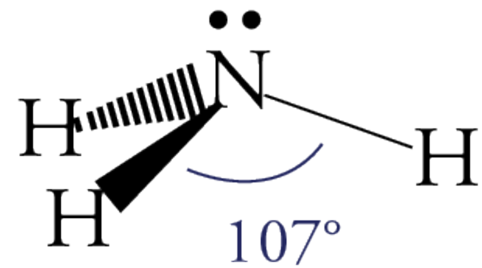
Geometric Sketch

Ammonia, NH_3

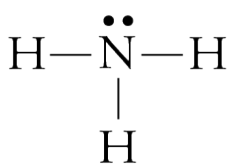




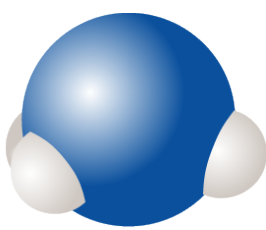
Electron group geometry (tetrahedral)



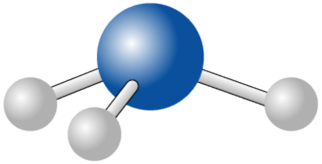
Molecular geometry (trigonal pyramid)



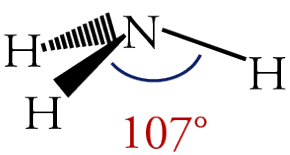
Lewis structure



Space-filling model

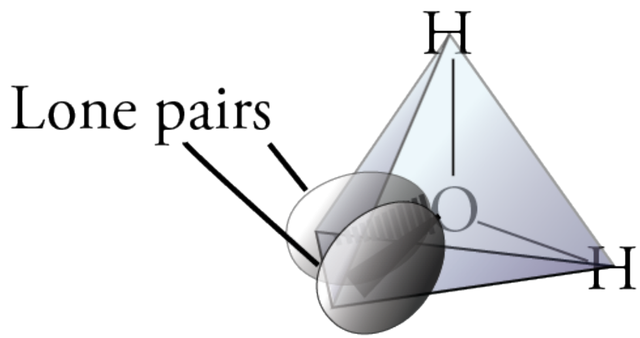


Ball-and-stick model



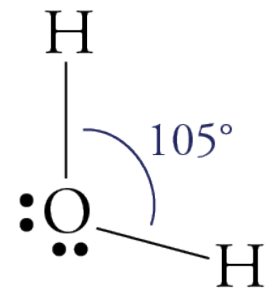
Geometric sketch

Water, H_2O

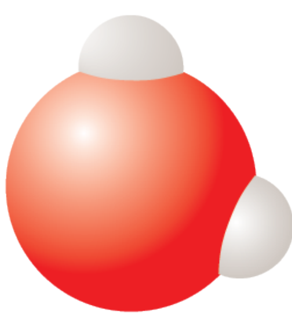


Electron group geometry
(tetrahedral)

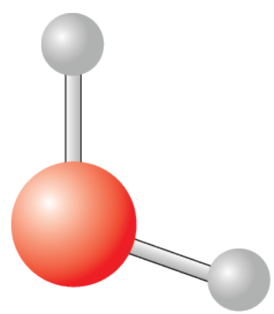
$H-\ddot{\underset{\cdot\cdot}{O}}-H$



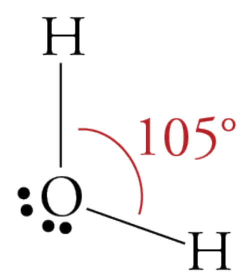
Molecular geometry
(bent)



Space-filling model

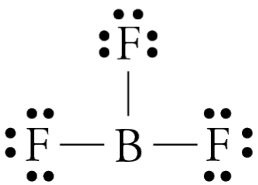


Ball-and-stick model

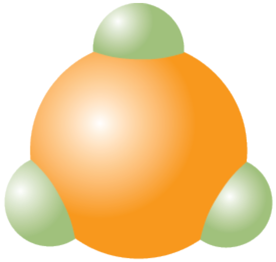


Geometric Sketch

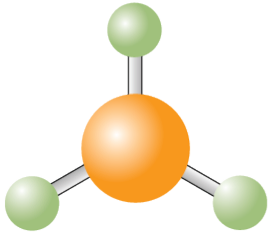
Trigonal Planar Geometry – BF_3



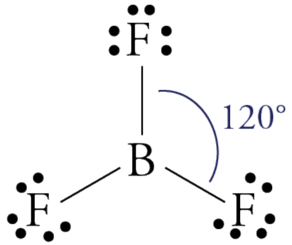
Lewis structure



Space-filling model

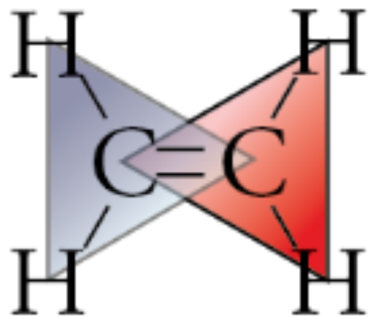


Ball-and-stick model

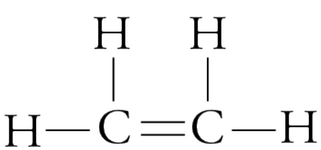


Geometric Sketch

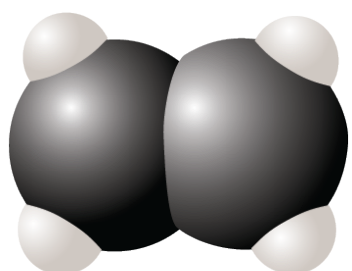
Ethene
(ethylene)



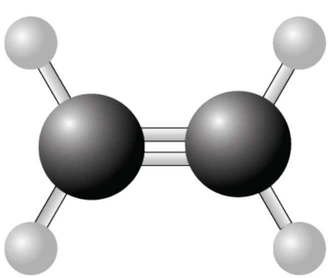
Trigonal planar
geometry around
each carbon



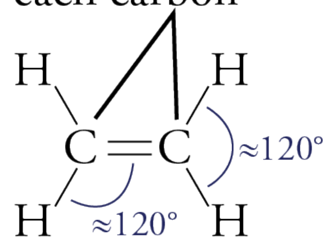
Lewis structure



Space-filling model

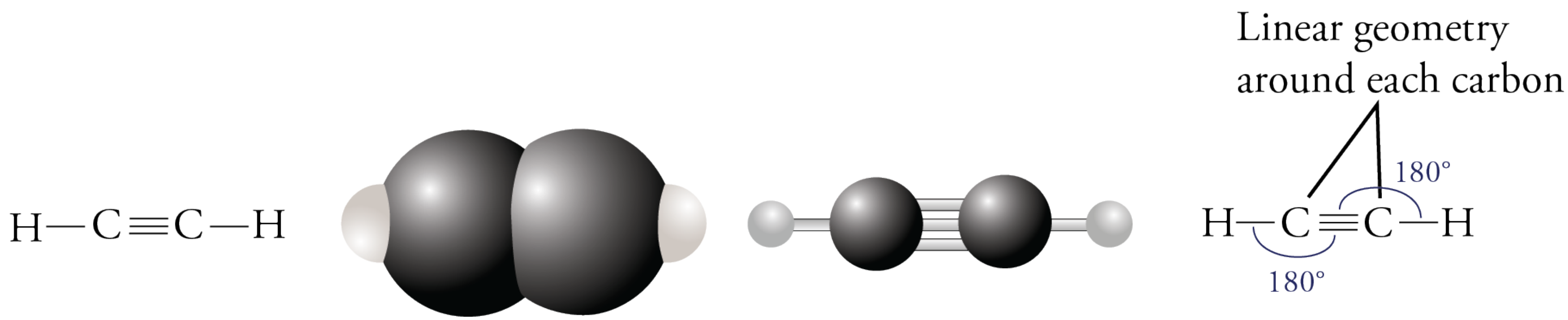


Ball-and-stick model



Geometric Sketch

Ethyne (acetylene) , C_2H_2



Lewis structure | Space-filling model | Ball-and-stick model | Geometric Sketch

Steps for Molecular Geometry

- **Step 1:** To determine the name of the electron group geometry around each atom that is attached to two or more atoms, count the number of electron groups around each atom and apply the guidelines found on Table 5.2.
- **Step 2:** Use one or more of the geometric sketches shown on Table 5.2 for the geometric sketch of your molecule.

Steps for Molecular Geometry (cont.)

- **Step 3:** To determine the name of the molecular geometry around each atom that has two or more atoms attached to it, count the number of bond groups and lone pairs, and then apply the guidelines found on Table 5.2.