

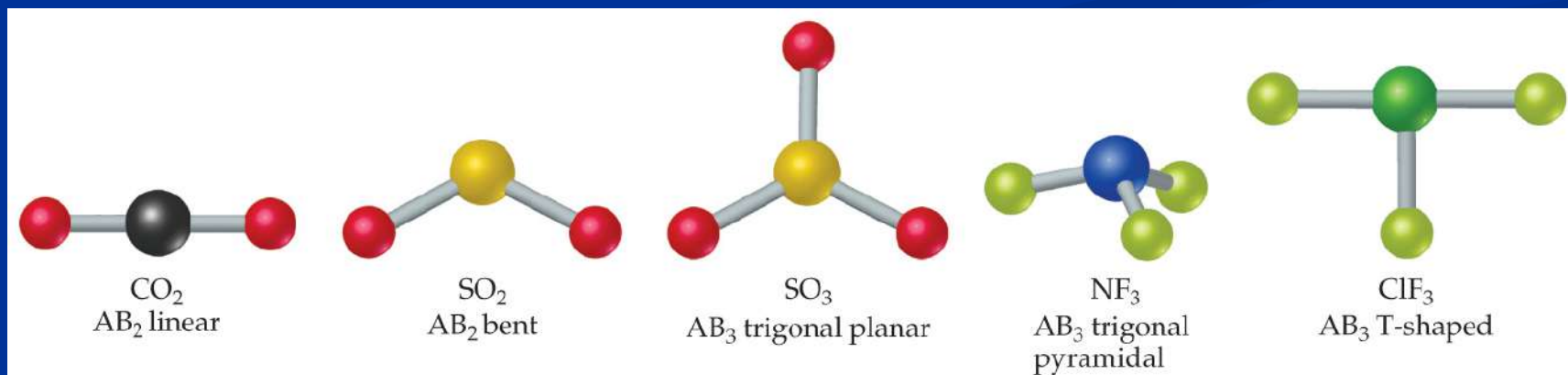
Chapter 9

Molecular Geometry and Bonding Theories

9.1 Molecular Shapes

Molecular Shapes

- Lewis Structures show bonding and lone pairs, but do *not* denote shape.
- However, we *use* Lewis Structures to help us determine shapes.
- Here we see some common shapes for molecules with two or three atoms connected to a central atom.

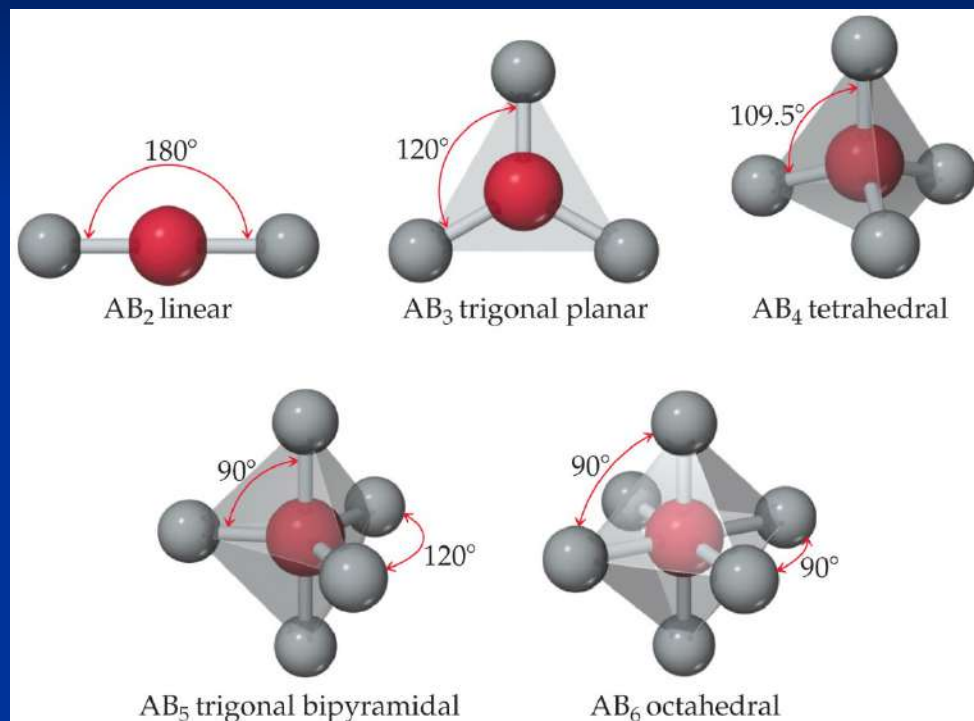


What Determines the Shape of a Molecule?

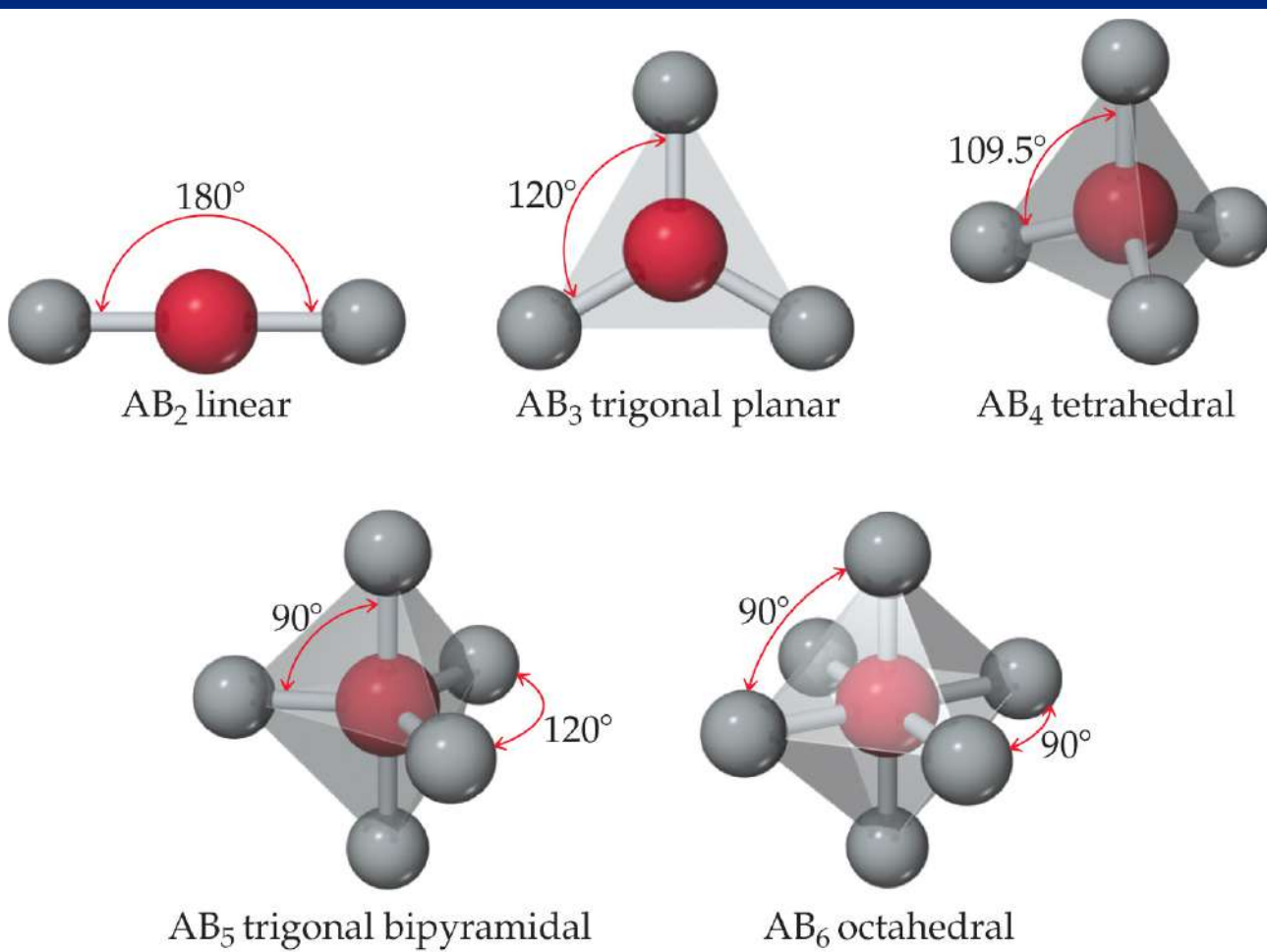
- Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.

- By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.

- This is the Valence-Shell Electron-Pair Repulsion (VSEPR) model.

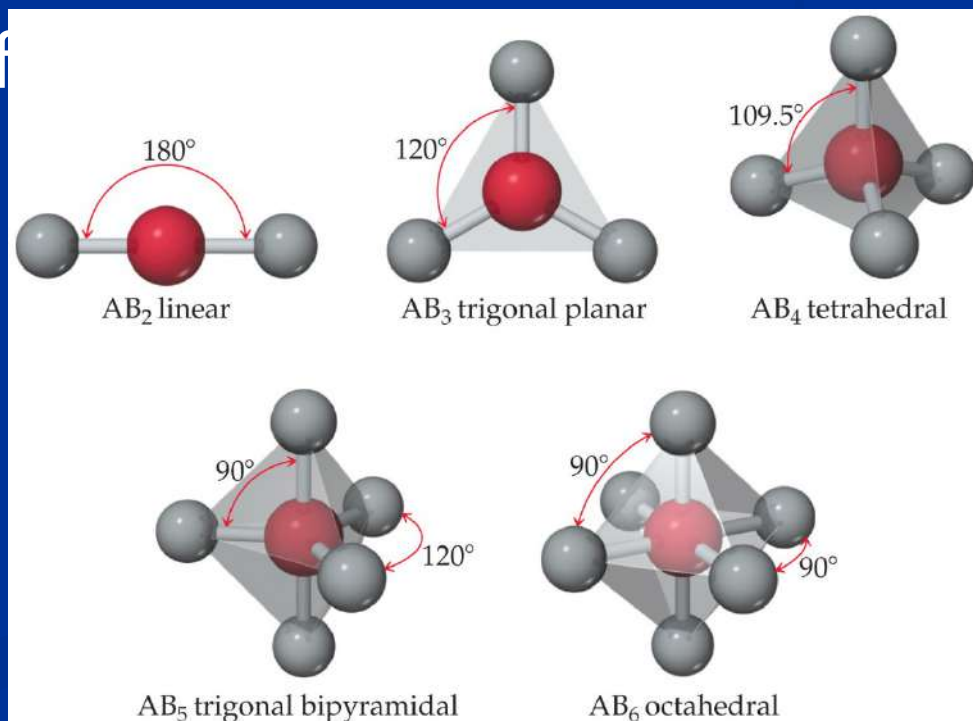


Which of these molecular shapes do you expect for the SF_6 molecule?

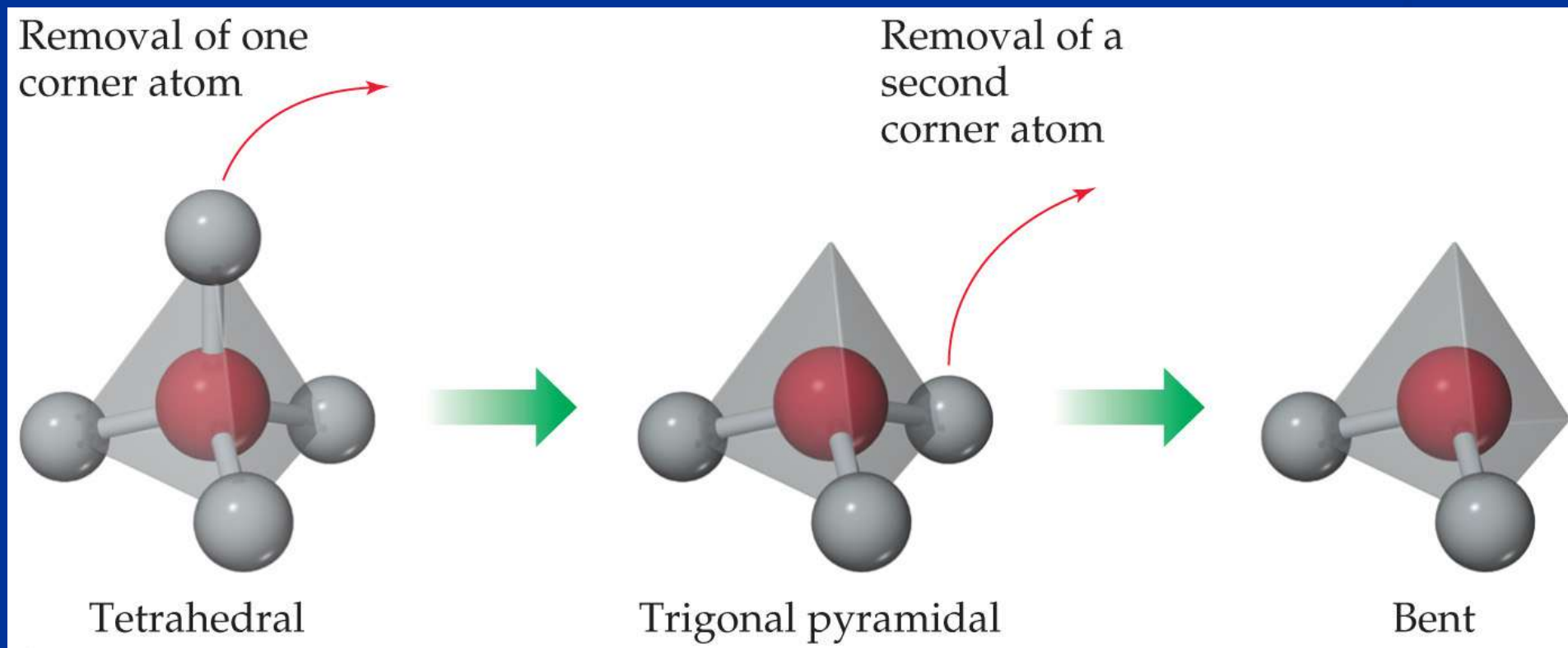


In addition to tetrahedral, another common shape for AB_4 molecules is *square planar*. All five atoms lie in the same plane, with the B atoms at the corners of a square and the A atom at the center of the square. Which shape in Figure 9.3 could lead to a square-planar shape upon removal of

- a. Trigonal planar
- b. Tetrahedral
- c. Trigonal bipyramidal
- d. Octahedral

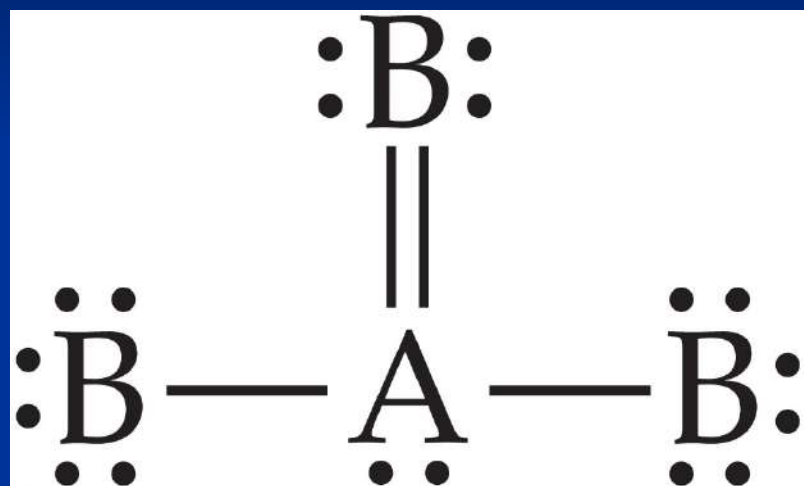


In going from the tetrahedral shape to the bent shape, does it matter which two of the atoms we choose to remove?



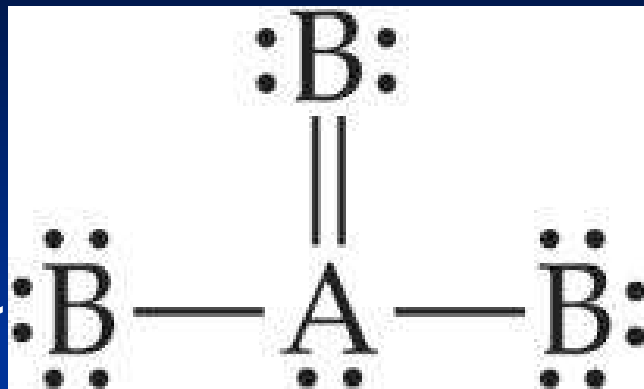
9.2 The VSEPR Model

Electron Domains



- We can refer to the directions to which electrons point as **electron domains**. This is true whether there is one or more electron pairs pointing in that direction.
- The central atom in this molecule, A, has four electron domains.

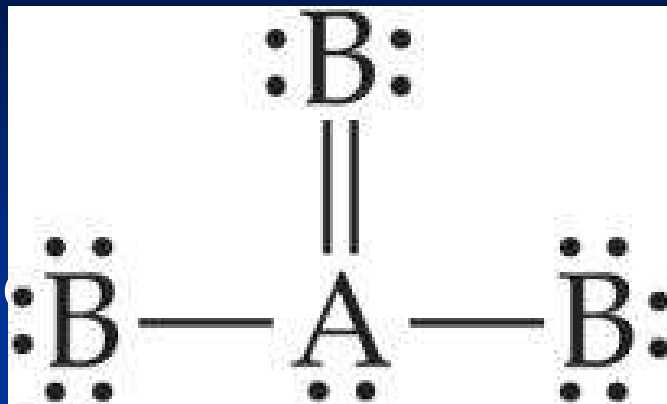
Suppose a particular AB_3 molecule has the resonance structure



Does this structure follow the octet rule?

- a. No, there are 10 electrons around A.
- b. Yes, there are 8 electrons around A.
- c. Yes, there are three bonds and one electron pair around A.
- d. Yes, there are four bonds around A.

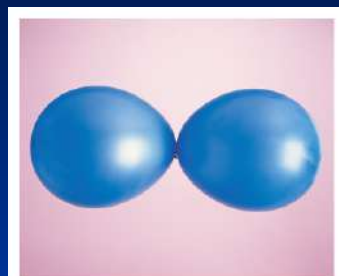
Suppose a particular AB_3 molecule has the resonance structure



How many electron domains are there around the A atom?

- a. One electron domain
- b. Two electron domains
- c. Three electron domains
- d. Four electron domains

Valence-Shell Electron-Pair Repulsion (VSEPR) Model



Two balloons
linear orientation



Three balloons
trigonal-planar orientation



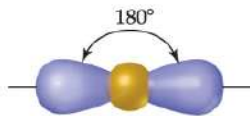
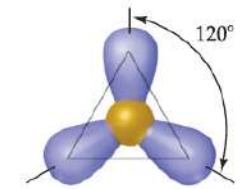
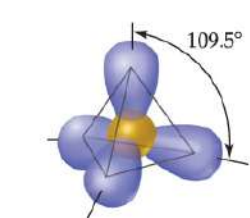
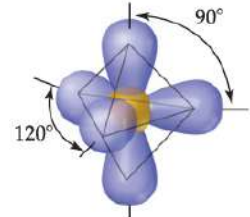
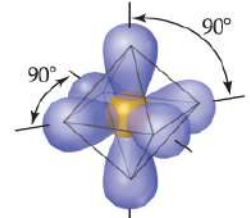
Four balloons
tetrahedral orientation

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

(The balloon analogy in the figure to the left demonstrates the maximum distances, which minimize repulsions.)

Electron-Domain Geometries

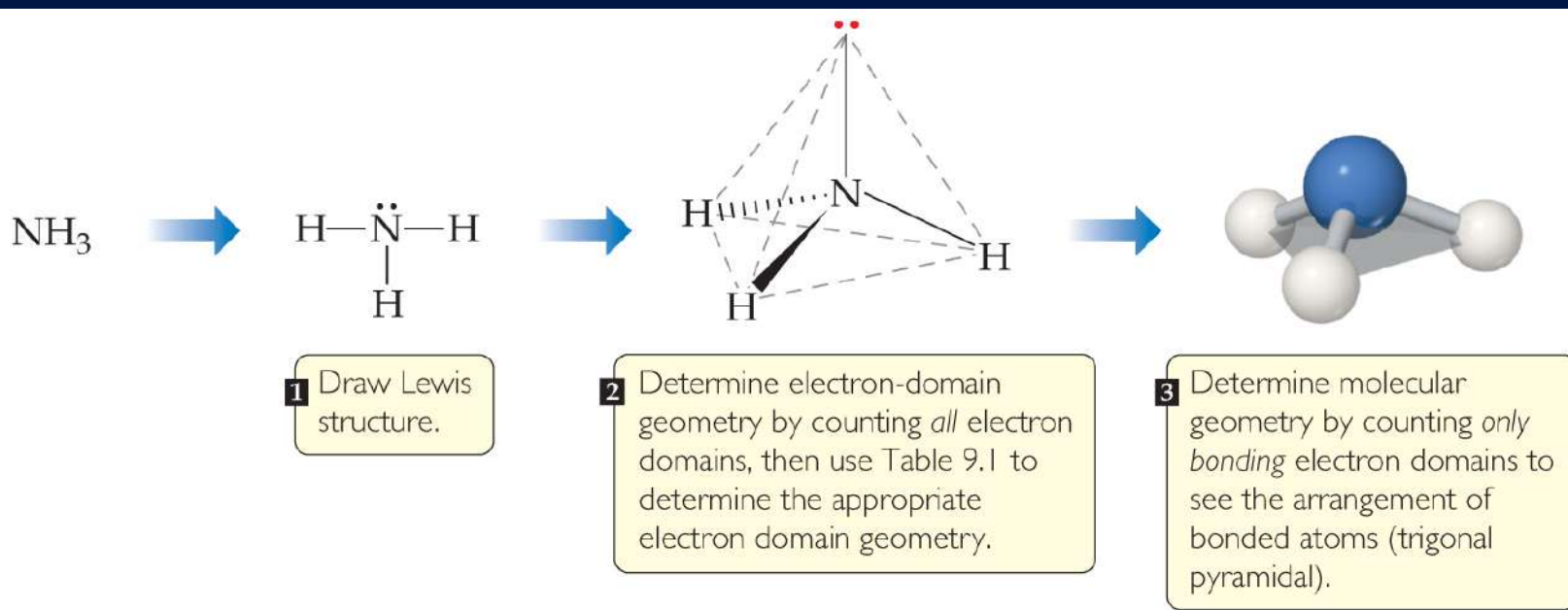
Table 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

■ The Table shows the electron-domain geometries for two through six electron domains around a central atom.

■ To determine the electron-domain geometry, count the total number of lone pairs, single, double, and triple bonds on the central atom.

Molecular Geometries



- Once you have determined the electron-domain geometry, use the arrangement of the bonded atoms to determine the **molecular geometry**.
- Tables 9.2 and 9.3 show the potential molecular geometries. We will look at each electron domain to see what molecular geometries are possible.

From the standpoint of the VSEPR model, what do nonbonding electron pairs, single bonds, and multiple bonds have in common?

- a. There are no common features.
- b. Each occurs about the central atom only.
- c. Each represents a single electron domain.
- d. All exist when a particular Lewis structure is drawn.

Linear Electron Domain

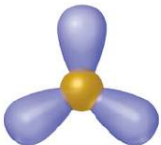
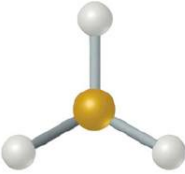
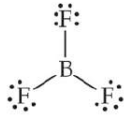
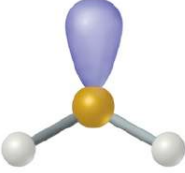
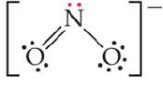
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$

- In the linear domain, there is only one molecular geometry: 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 Electron Domain

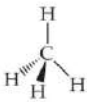
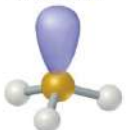
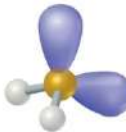
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

- There are two molecular geometries:
 - trigonal planar, if all electron domains are bonding, and
 - bent, if one of the domains is a nonbonding pair.

Tetrahedral Electron Domain

Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

- There are three molecular geometries:
 - tetrahedral, if all are bonding pairs,
 - trigonal pyramidal, if one is a nonbonding pair, and
 - bent, if there are two nonbonding pairs.

Sample Exercise 9.1

- 1) Use the VSEPR model to predict the molecular geometry of
 - A) O_3
 - B) SnCl_3^-
- 2) Predict the electron-domain geometry and the molecular geometry for
 - A) SeCl_2
 - B) CO_3^{2-}

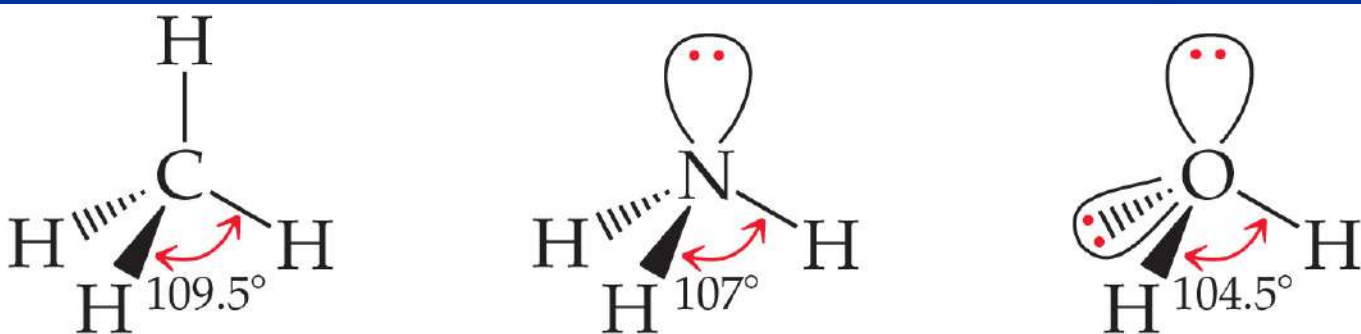
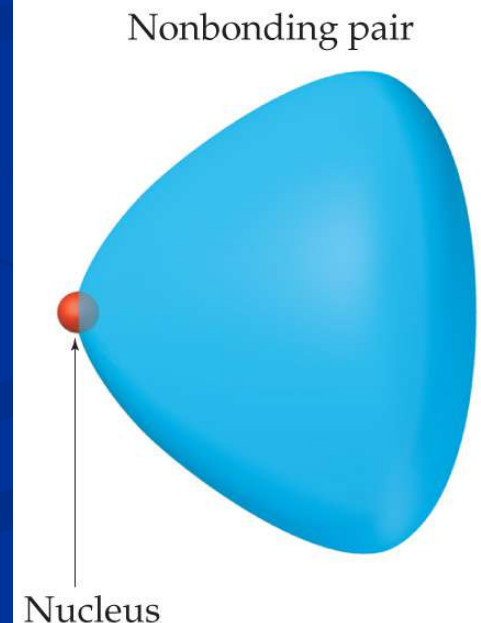
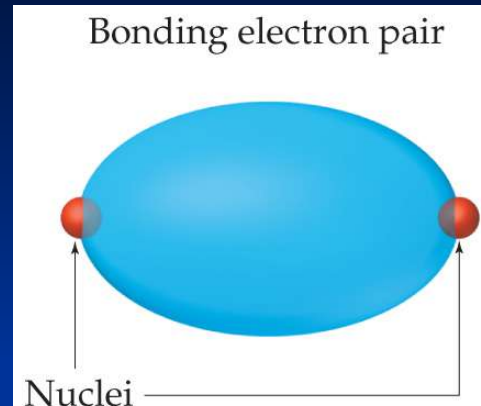
Practice Exercise 1

Consider the following AB_3 molecules and ions: PCl_3 , SO_3 , $AlCl_3$, SO_3^{2-} , and CH_3^+ . How many of these molecules and ions do you predict to have a trigonal-planar molecular geometry?

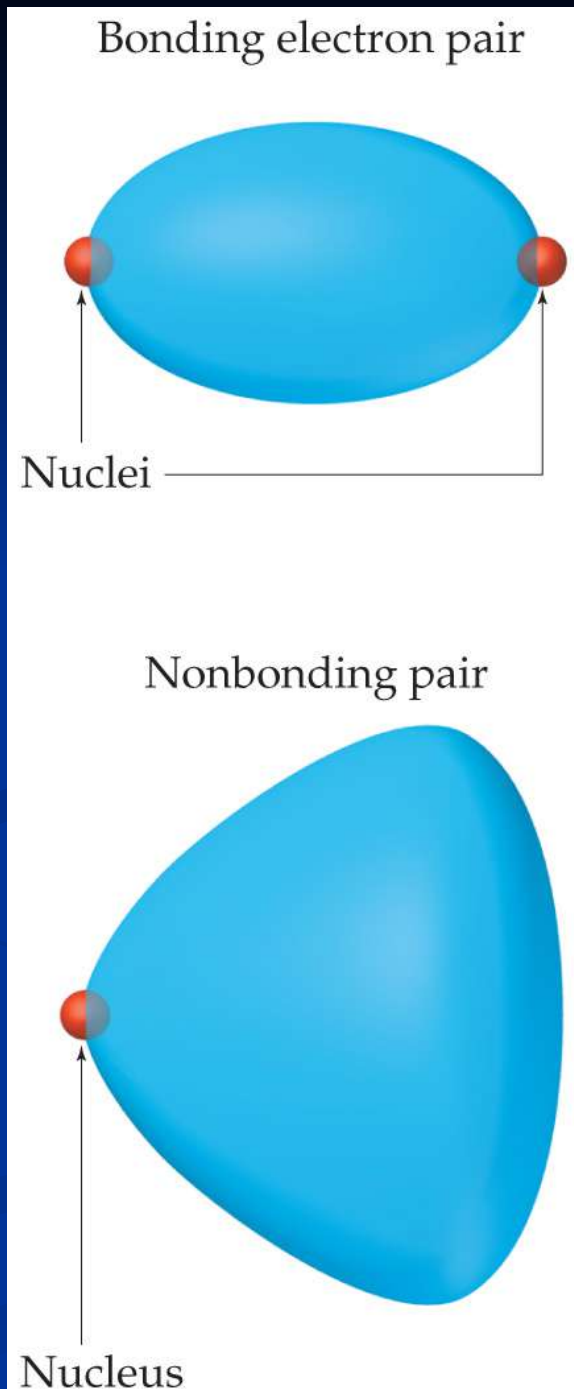
- (a) 1
- (b) 2
- (c) 3
- (d) 4
- (e) 5

Nonbonding Pairs and Bond Angle

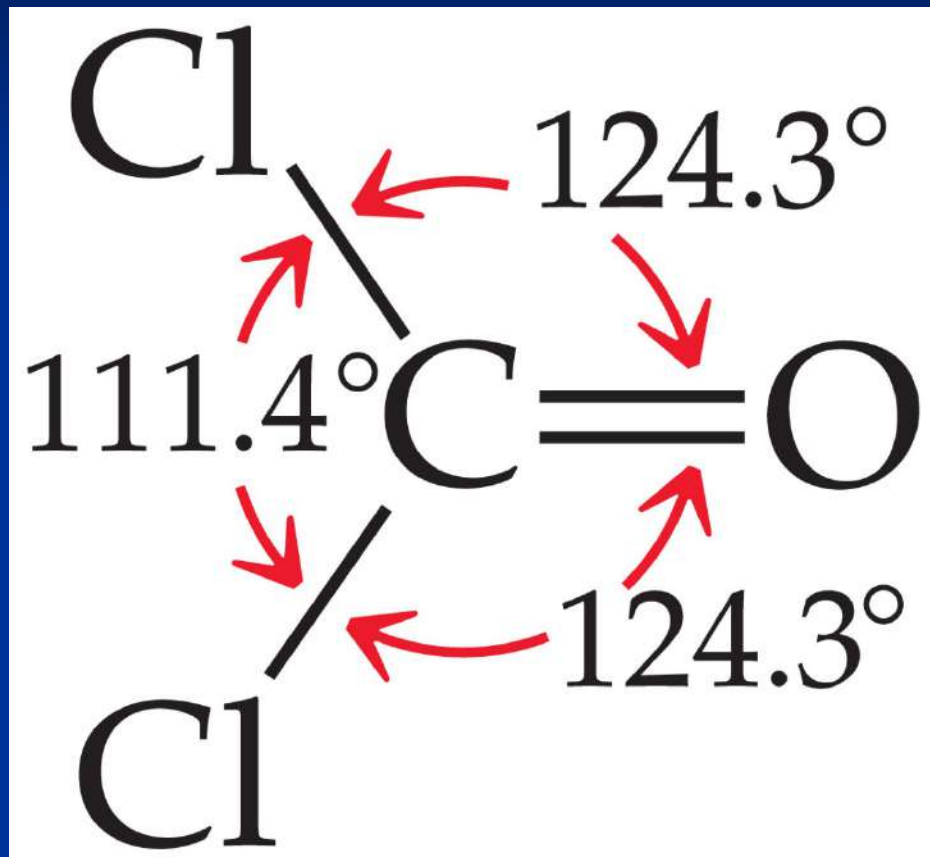
- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to compress bond angles.



- Why is the volume occupied by the nonbonding electron pair domain larger than the volume occupied by the bonding domain?

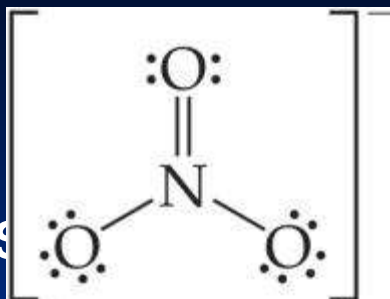


Multiple Bonds and Bond Angles



- Double and triple bonds have larger electron domains than single bonds.
- They exert a greater repulsive force than single bonds, making their bond angles greater.

One resonance structure of the nitrate ion is



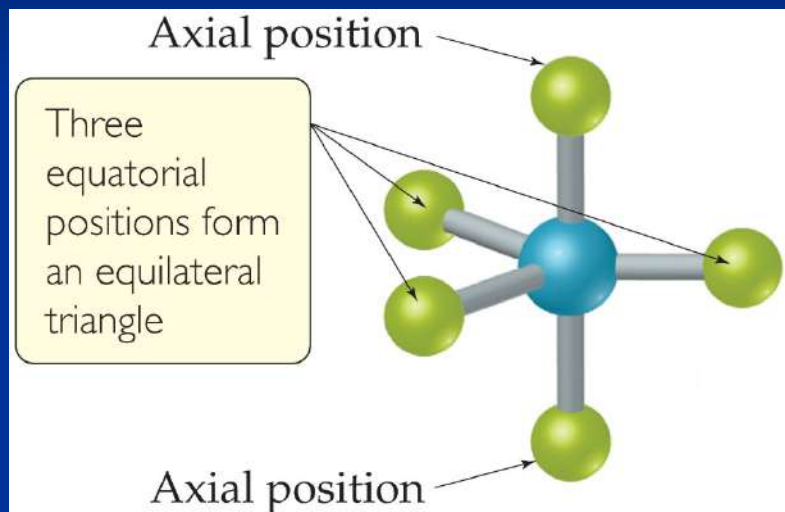
The bond angles are 120° . Is this observation consistent with the preceding discussion of the effect of multiple bonds on bond angles?

- No, the domain with the double bond should “push” the other two electron domains resulting in the bond angle between single bonds to less than 120° .
- Yes, the existence of resonance with three resonance structures equalizes repulsions between electron domains resulting in all bond angles equaling 120° .

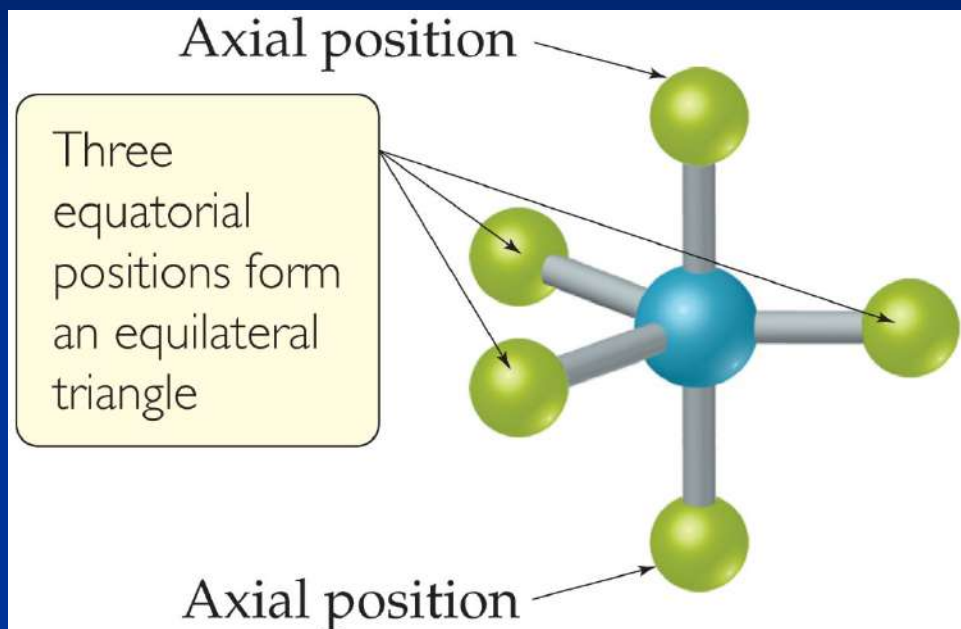
Expanding beyond the Octet Rule

- Remember that some elements can break the octet rule and make *more* than four bonds (or have more than four electron domains).
- The result is two more possible electron domains: five = trigonal bipyramidal; six = octahedral (as was seen in the slide on electron-domain geometries).

Trigonal Bipyramidal Electron Domain



- There are two distinct positions in this geometry:
 - Axial
 - Equatorial
- Lone pairs occupy equatorial positions.



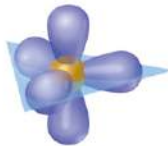
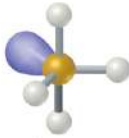
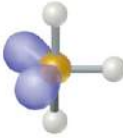
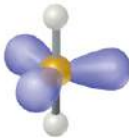
■ What is the bond angle formed by an axial atom, the central atom, and any equatorial atom?

Trigonal Bipyramidal Electron Domain

■ There are four distinct molecular geometries in this domain:

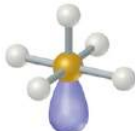
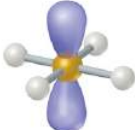
- Trigonal bipyramidal
- Seesaw
- T-shaped
- Linear

Table 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl ₅
		4	1	 Seesaw	SF ₄
		3	2	 T-shaped	ClF ₃
		2	3	 Linear	XeF ₂

Octahedral Electron Domain

Table 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF ₆
		5	1	 Square pyramidal	BrF ₅
		4	2	 Square planar	XeF ₄

■ All positions are equivalent in the octahedral domain.

■ There are three molecular geometries:

- Octahedral
- Square pyramidal
- Square planar

It might seem that a square-planar geometry of four electron domains around a central atom would be more favorable than a tetrahedron. Can you rationalize why the tetrahedron is preferred, based on angles between electron domains?

- a. Bond angles are not determined by a particular arrangement of electron domains.
- b. A tetrahedral arrangement of electron domains results in greater electron repulsions and a less favorable geometry than electron domains in a square planar geometry.
- c. A tetrahedral arrangement of electron domains results in smaller electron repulsions and a more favorable geometry than electron domains in a square planar geometry.
- d. A tetrahedral arrangement of electron domains results in no greater electron repulsions and no greater favorable geometry than electron domains in a square planar geometry.

Sample Exercise 9.2

■ 1) Use the VSEPR model to predict the molecular geometry of

■ A) SF_4

■ B) IF_5

Practice Exercise 1

A certain AB_4 molecule has a square-planar molecular geometry. Which of the following statements about the molecule is or are true?:

(i) The molecule has four electron domains about the central atom A.

(ii) The B—A—B angles between neighboring B atoms is 90° .

(iii) The molecule has two nonbonding pairs of electrons on atom A.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

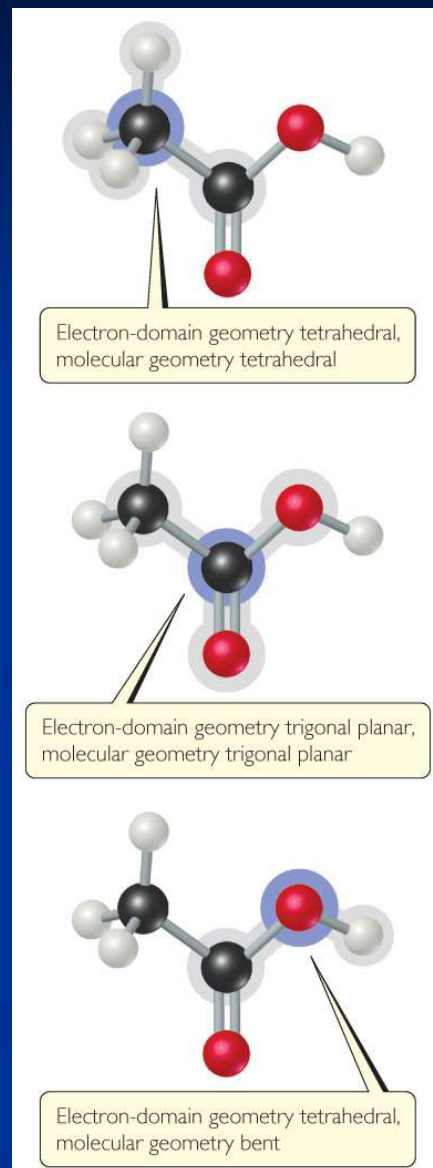
Practice Exercise 2

Predict the electron-domain and molecular geometries of

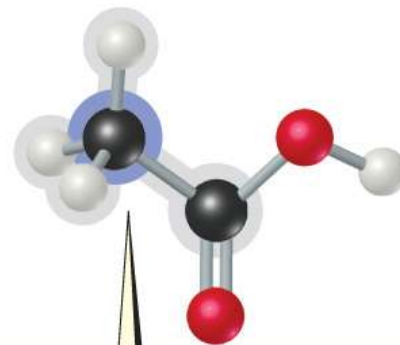


Shapes of Larger Molecules

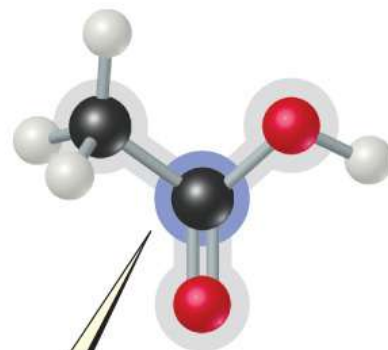
For larger molecules, look at the geometry about each atom rather than the molecule as a whole.



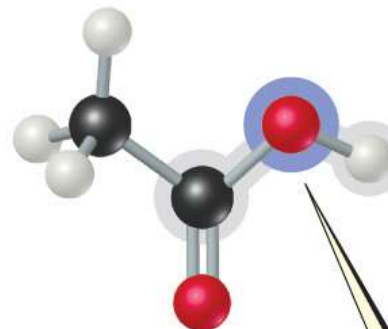
In the actual structure of acetic acid, which bond angle is expected to be the smallest?



Electron-domain geometry tetrahedral,
molecular geometry tetrahedral

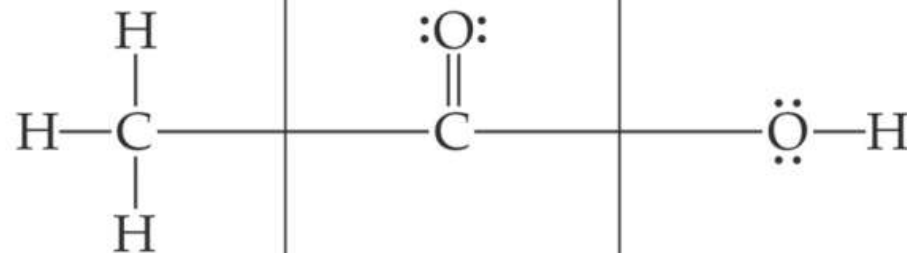
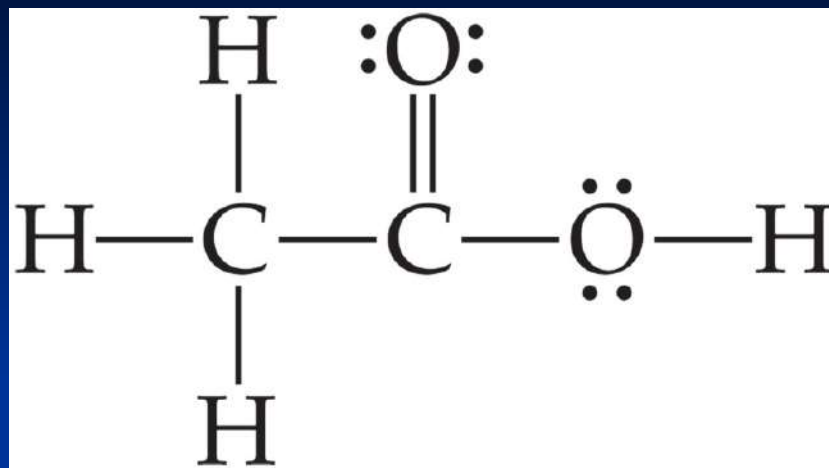


Electron-domain geometry trigonal planar,
molecular geometry trigonal planar



Electron-domain geometry tetrahedral,
molecular geometry bent

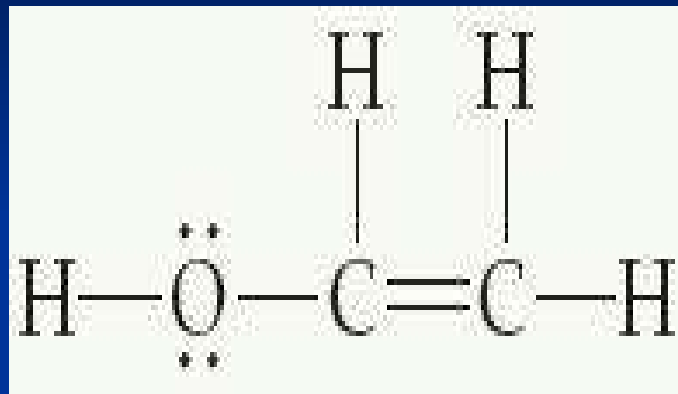
Larger Molecules



Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

Sample Exercise 9.3 Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule called *vinyl alcohol*:



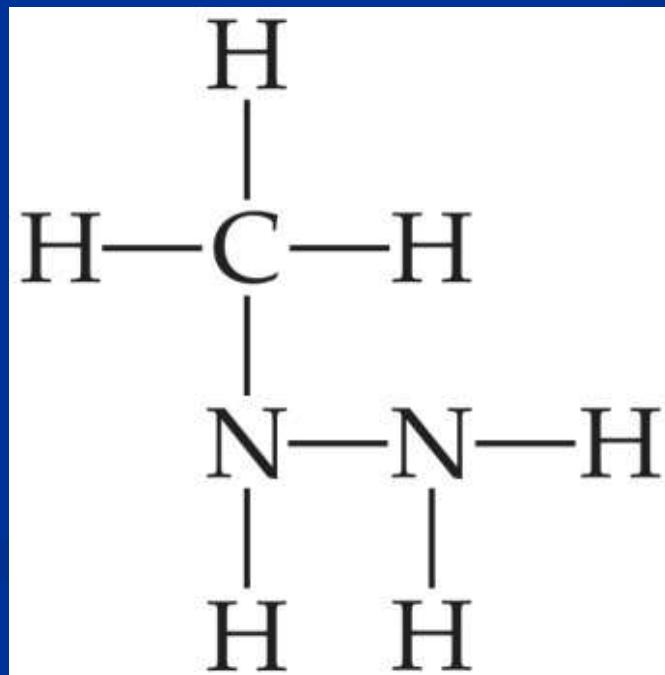
Predict the approximate values for the H—O—C and O—C—C bond angles in vinyl alcohol.

Practice Exercise 1

The atoms of the compound methylhydrazine, CH_6N_2 , which is used as a rocket propellant, are connected as follows (lone pairs are not shown):

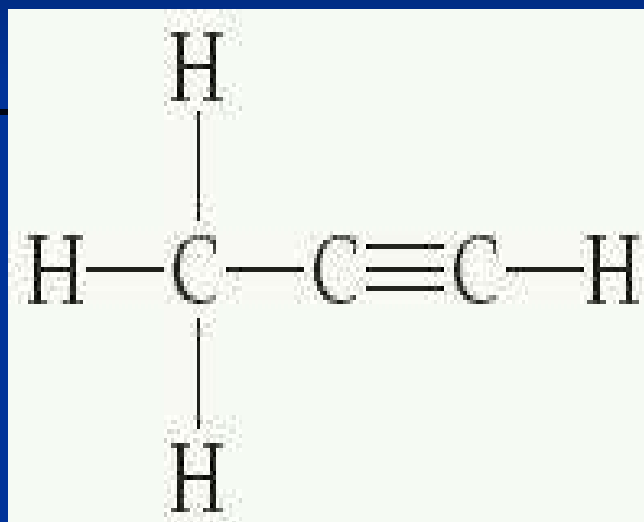
What do you predict for the ideal values of the C—N—N and H—N—H angles, respectively?

- (a) 109.5° and 109.5°
- (b) 109.5° and 120°
- (c) 120° and 109.5°
- (d) 120° and 120°
- (e) None of the above



Practice Exercise 2

Predict the H—C—H and C—C—C bond angles in the following molecule, called *propyne*:



9.3 Molecular Shape and Molecular Polarity

Polarity of Molecules

Ask yourself:

COVALENT or IONIC? If COVALENT:

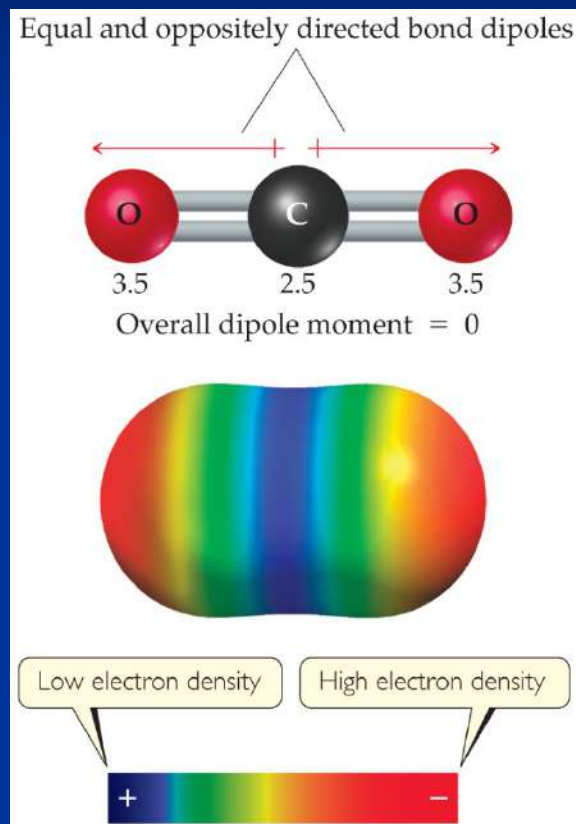
Are the BONDS polar?

- a. NO: The molecule is NONPOLAR!
- b. YES: Continue—Do the AVERAGE position of $\delta+$ and $\delta-$ coincide?
- 3) YES: The molecule is NONPOLAR.
- 4) NO: The molecule is POLAR.

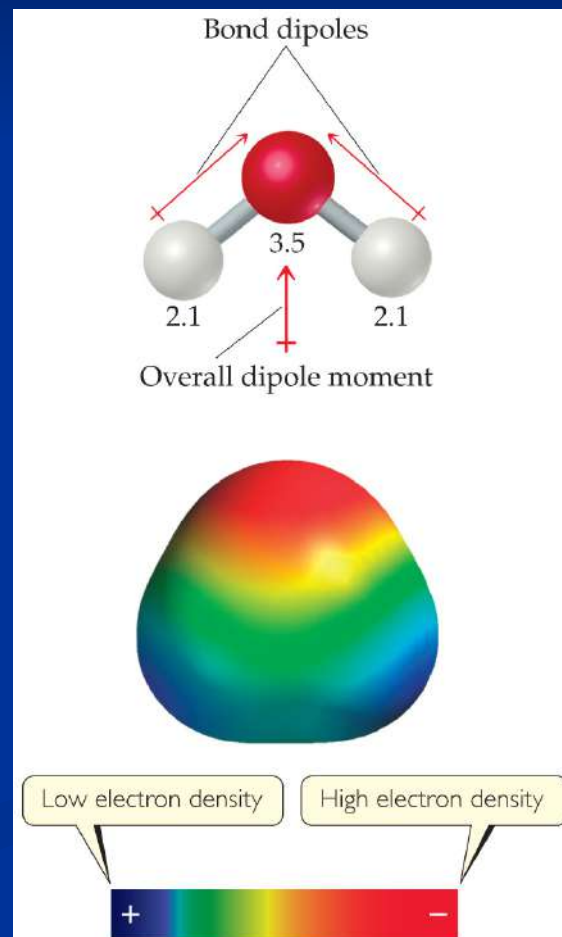
NOTE: Different atoms attached to the central atom have different polarity of bonds.

Comparison of the Polarity of Two Molecules

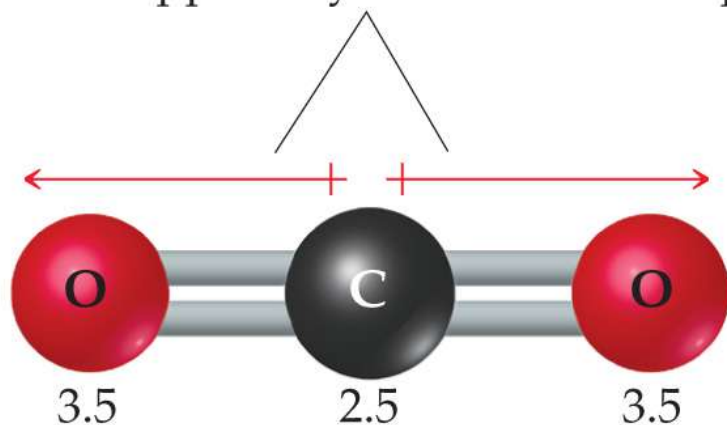
A NONPOLAR molecule



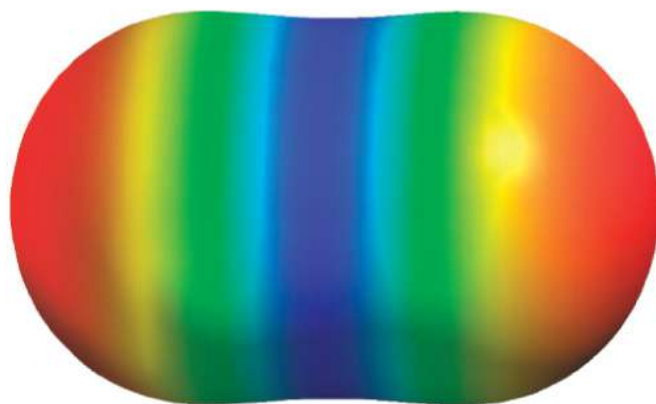
A POLAR molecule



Equal and oppositely directed bond dipoles



Overall dipole moment = 0



Low electron density

High electron density



What is the
sum of the
two red
vectors at the
top of the
figure?

The molecule $\text{O}=\text{C}=\text{S}$ is linear and has a Lewis structure analogous to that of CO_2 . Would you expect this molecule to be nonpolar?

- a. Yes, because COS has different elements than in CO_2 .
- b. No, because COS is linear.
- c. Yes, because O and S have different electronegativities, and CO and CS bond dipoles do not cancel each other.
- d. No, because O and S have similar electronegativities, and CO and CS bond dipoles cancel each other.

■ For AB_n molecules where B is the same atom, the following molecular geometries will be nonpolar:

■ Linear (AB_2)

■ Trigonal planar (AB_3)

■ Tetrahedral (AB_4)

■ Square planar (AB_4E_2)

■ Trigonal bipyramidal (AB_5)

■ Octahedral (AB_6)

Sample Exercise 9.4

■ Predict whether the following molecules are polar or nonpolar:



Practice Exercise 1

Consider an AB_3 molecule in which A and B differ in electronegativity. You are told that the molecule has an overall dipole moment of zero. Which of the following could be the molecular geometry of the molecule?

- (a) Trigonal pyramidal
- (b) Trigonal planar
- (c) T-shaped
- (d) Tetrahedral
- (e) More than one of the above

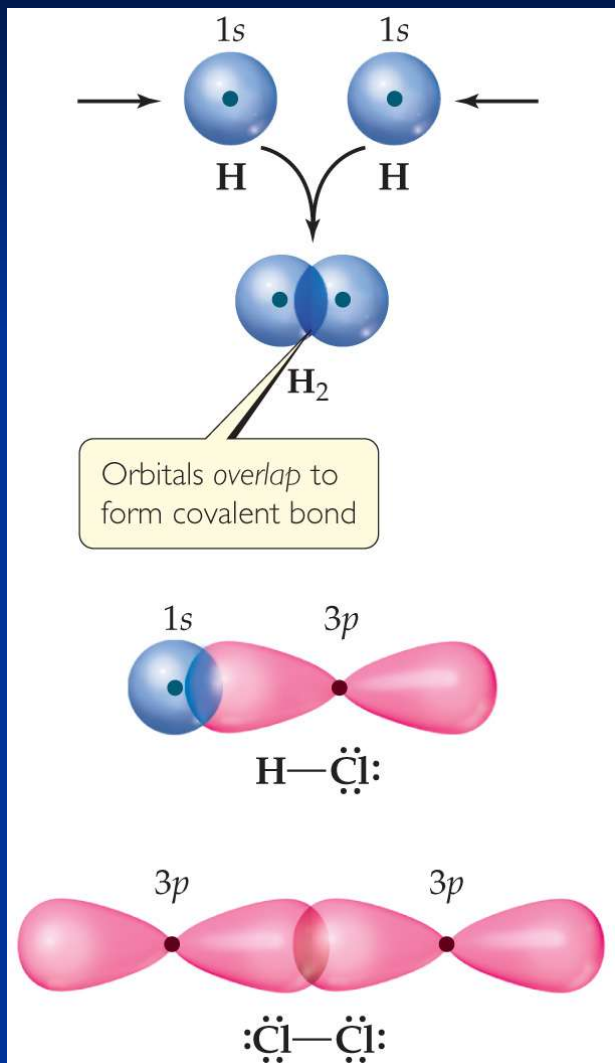
Practice Exercise 2

Determine whether the following molecules are polar or nonpolar:

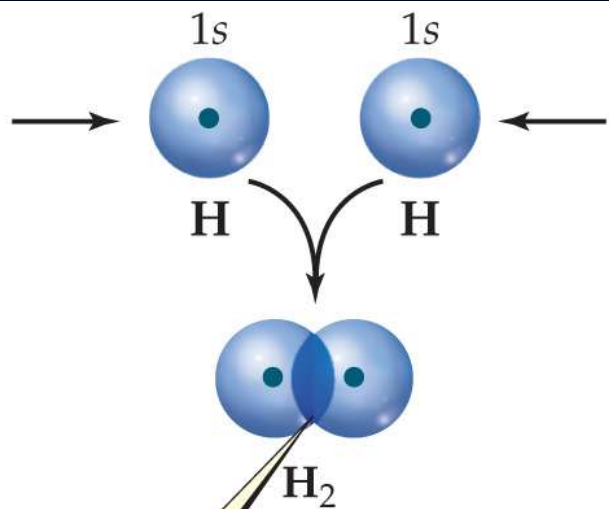


9.4 Covalent Bonding and Orbital Overlap

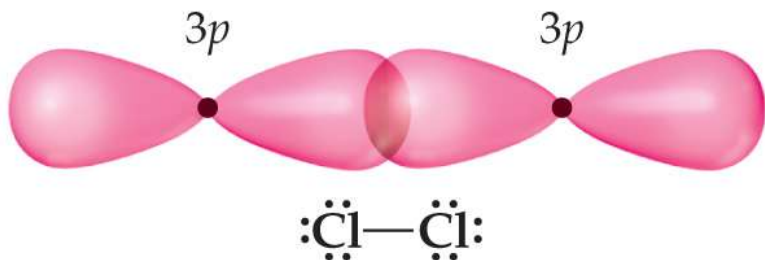
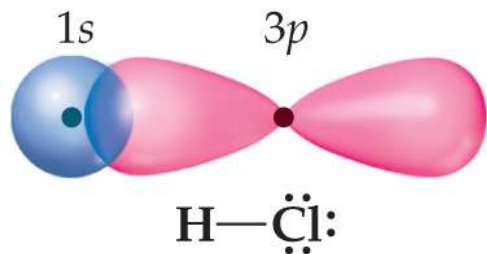
Valence-Bond Theory



- In Valence-Bond Theory, electrons of two atoms begin to occupy the same space.
- This is called “overlap” of orbitals.
- The sharing of space between two electrons of opposite spin results in a covalent bond.



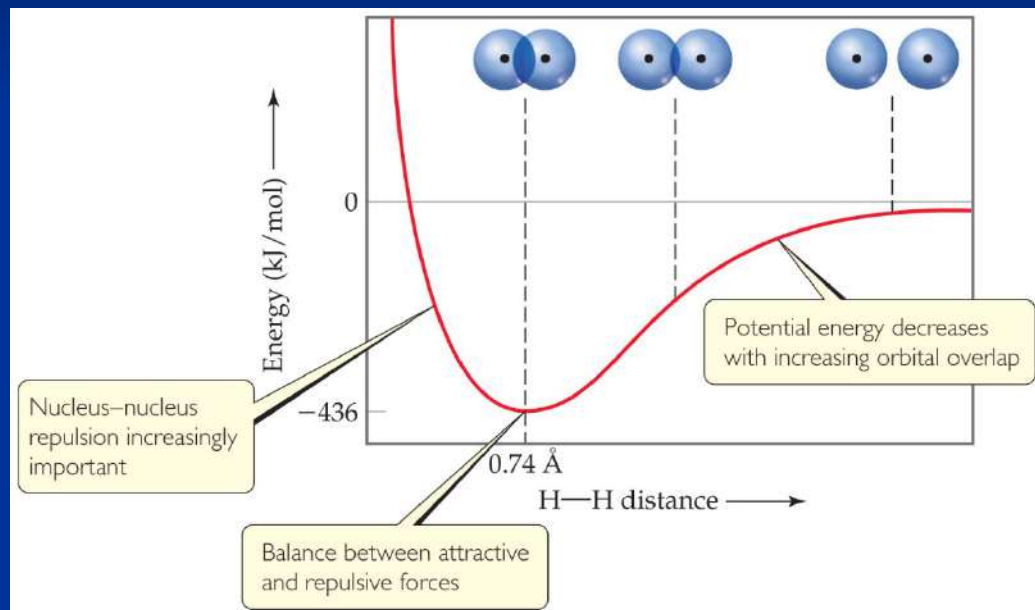
Orbitals overlap to form covalent bond



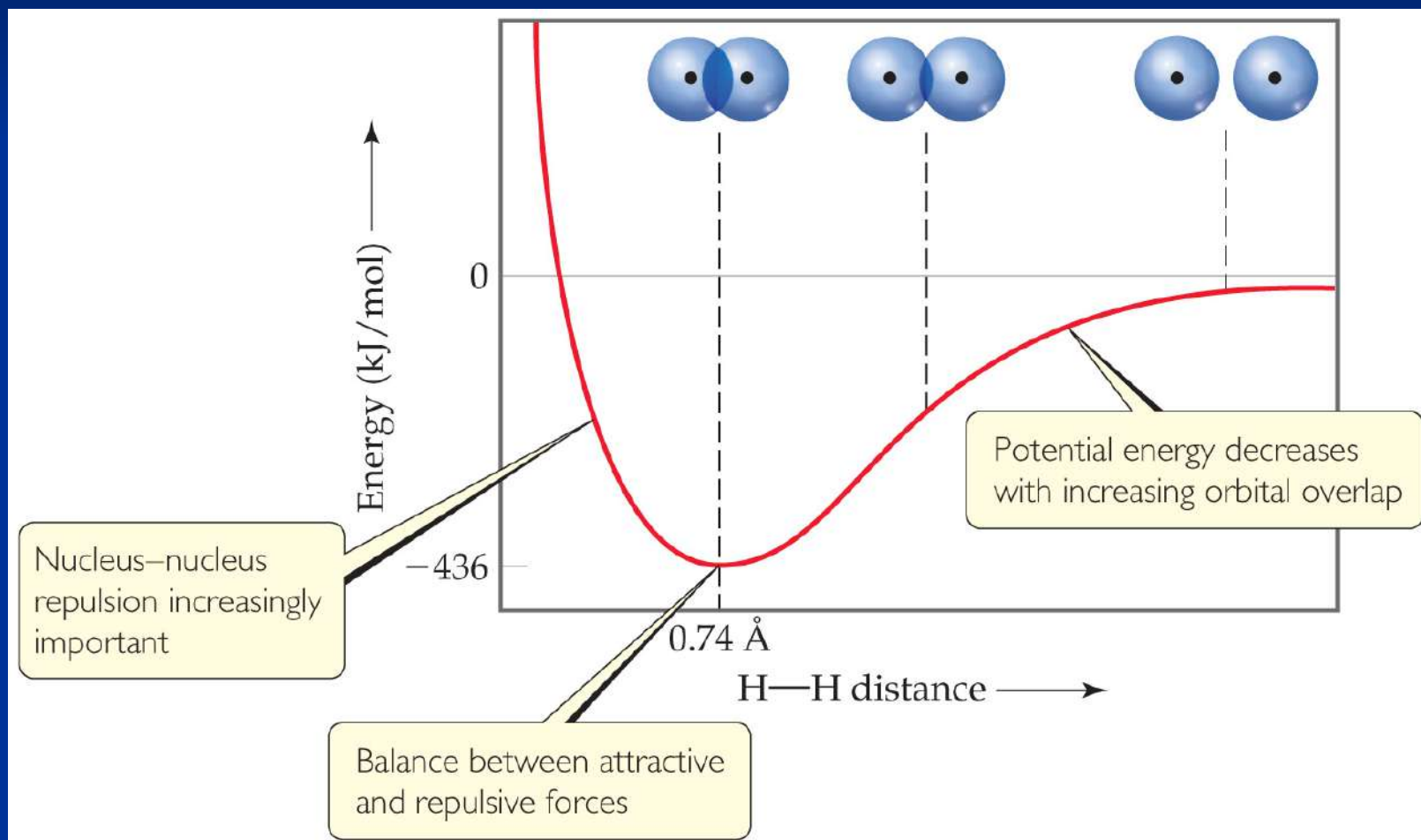
■ How does the notion of overlap explain why the bond in HCl is longer than the bond in H_2 ?

Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together until a balance is reached between the like charge repulsions and the electron-nucleus attraction.
- Atoms can't get too close because the internuclear repulsions get too great.



On the left part of the curve the potential energy rises above zero.
What causes this to happen?



9.5 Hybrid Orbitals

VSEPR and Hybrid Orbitals

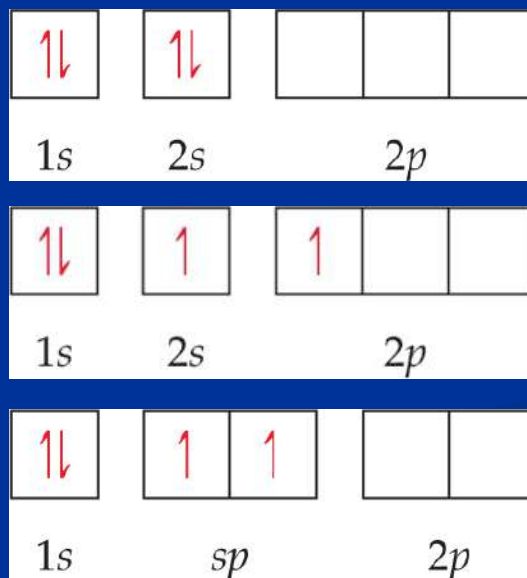
- VSEPR predicts shapes of molecules very well.
- How does that fit with orbitals?
- Let's use H₂O as an example:
- If we draw the best Lewis structure to assign VSEPR, it becomes bent.
- If we look at oxygen, its electron configuration is $1s^2 2s^2 2p^4$. If it shares two electrons to fill its valence shell, they should be in $2p$.
- Wouldn't that make the angle 90° ?
- Why is it 104.5° ?

Hybrid Orbitals

- **Hybrid orbitals** form by “mixing” of atomic orbitals to create new orbitals of equal energy, called degenerate orbitals.
- When two orbitals “mix” they create two orbitals; when three orbitals mix, they create three orbitals; etc.

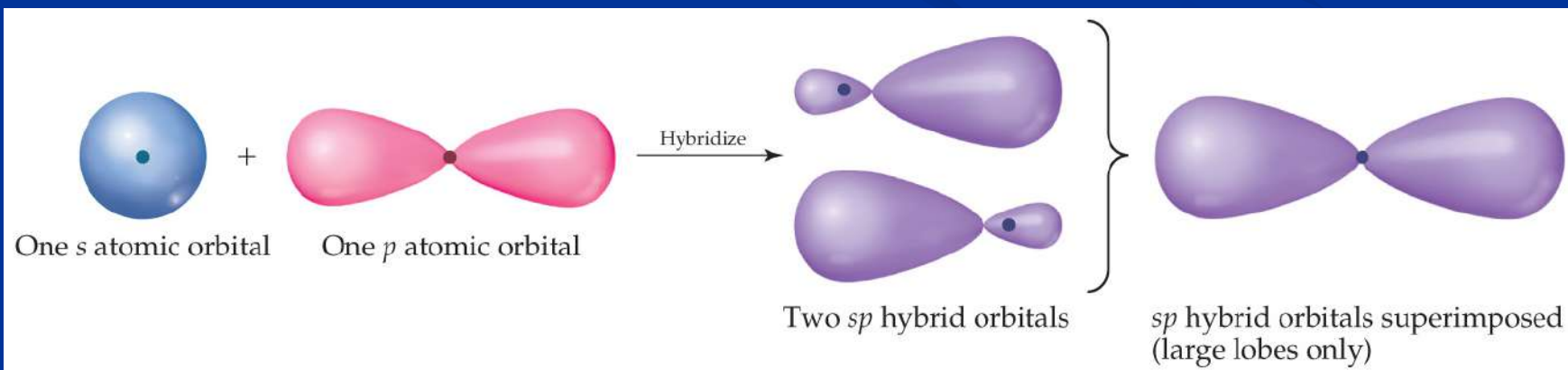
Be—*sp* hybridization

- When we look at the orbital diagram for beryllium (Be), we see that there are only paired electrons in full sub-levels.
- Be makes electron deficient compounds with two bonds for Be. Why? *sp* hybridization (mixing of one *s* orbital and one *p* orbital)



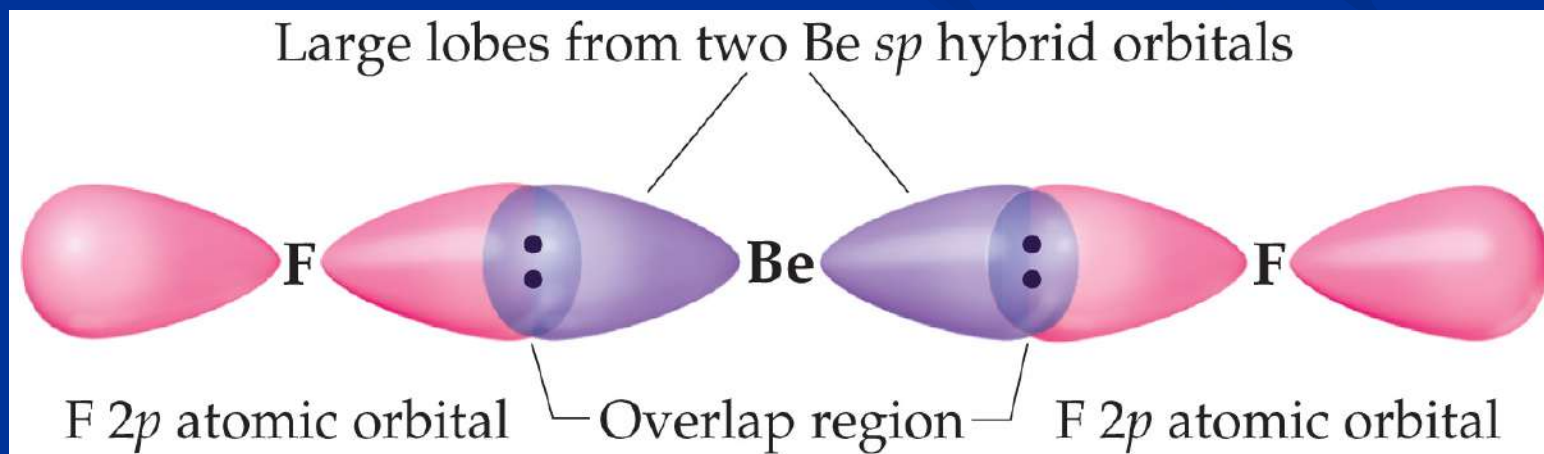
sp Orbitals

- Mixing the *s* and *p* orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
- These *sp* hybrid orbitals have two lobes like a *p* orbital.
- One of the lobes is larger and more rounded, as is the *s* orbital.



Position of *sp* Orbitals

- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of Be compounds (like BeF_2) and VSEPR: linear.

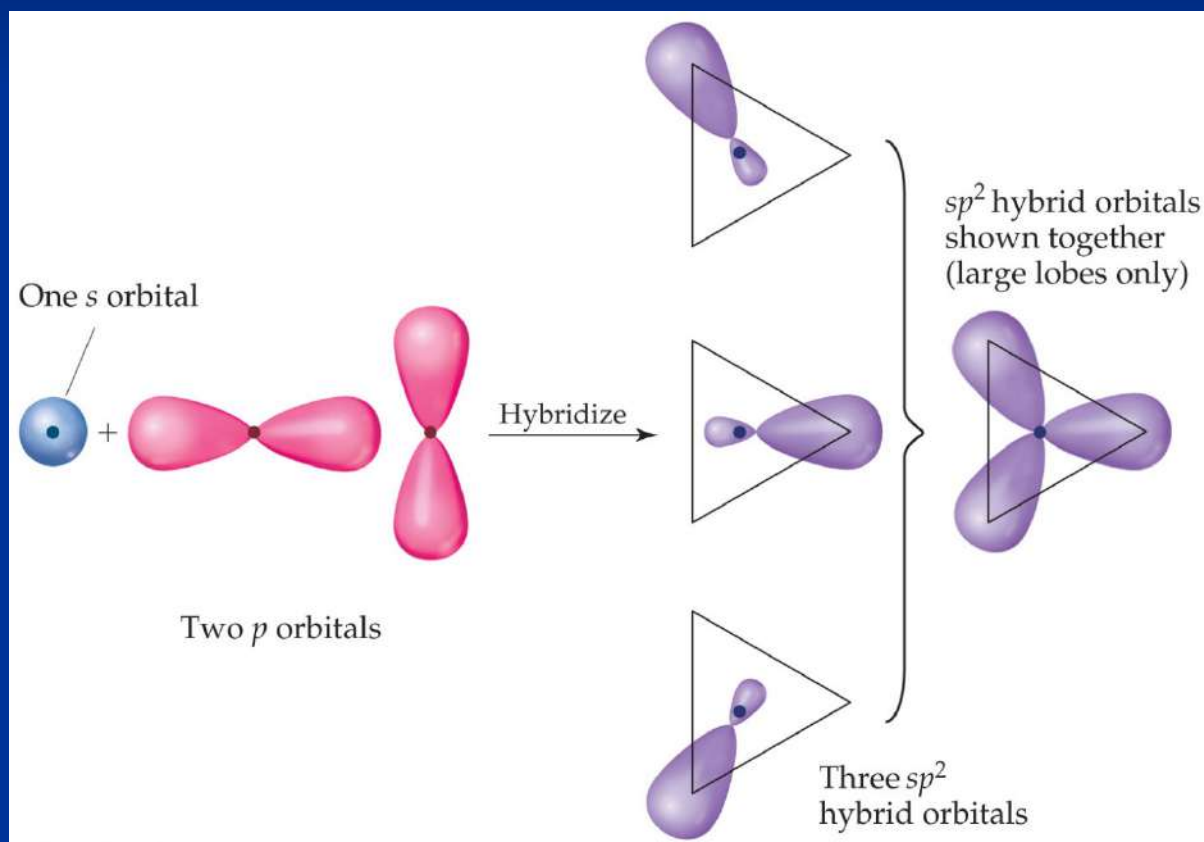


What is the orientation of the two unhybridized p orbitals on Be with respect to the two Be—F bonds?

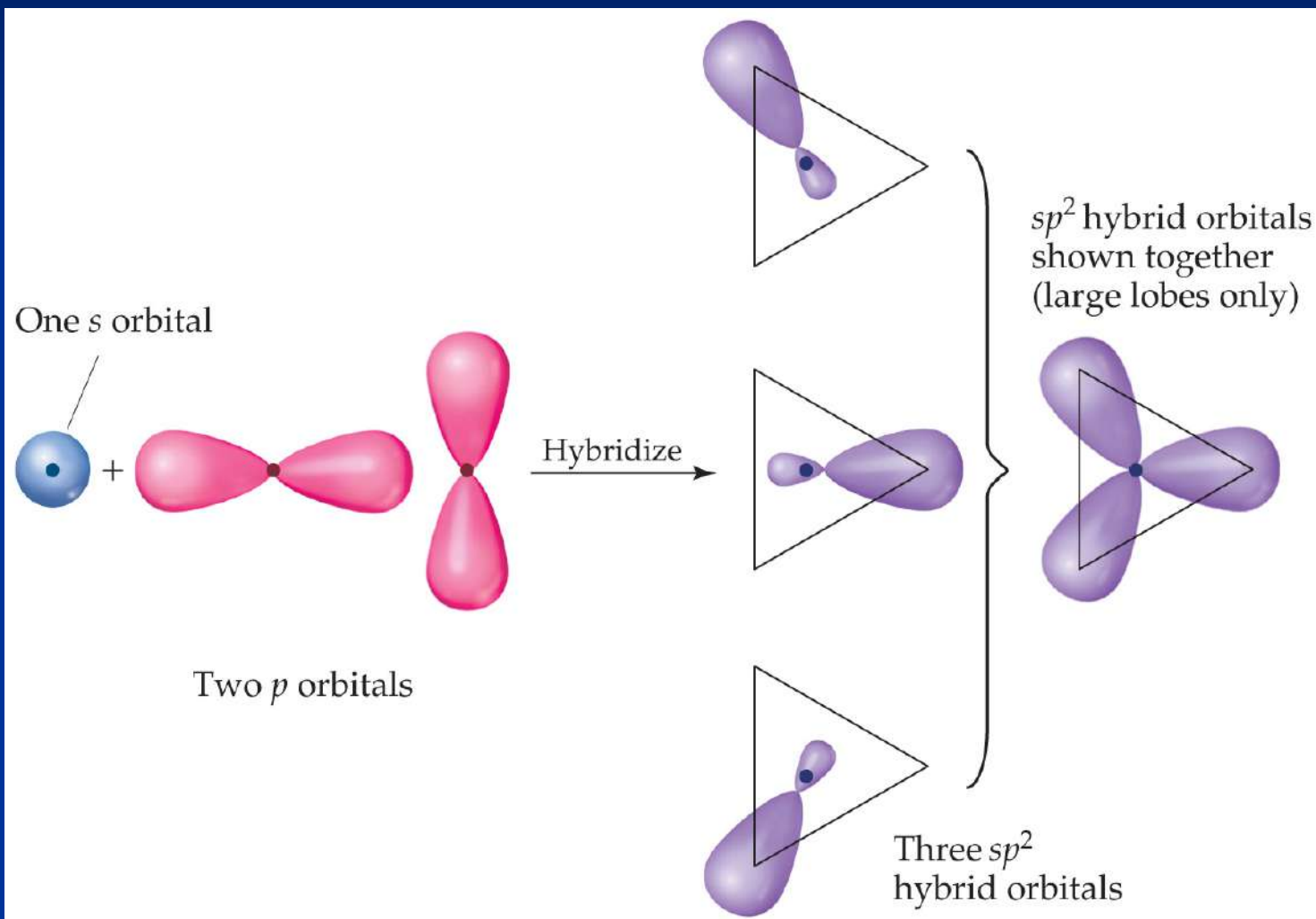
- a. Both p orbitals are parallel to the Be—F bonds.
- b. Both p orbitals intersect the Be—F bonds.
- c. Both p orbitals are at an angle of 120° to the Be—F bonds.
- d. Both p orbitals are perpendicular to the Be—F bonds.

Boron—Three Electron Domains Gives sp^2 Hybridization

Using a similar model for boron leads to three degenerate sp^2 orbitals.



What is the angle formed between the large lobes of the three sp^2 hybrid orbitals?

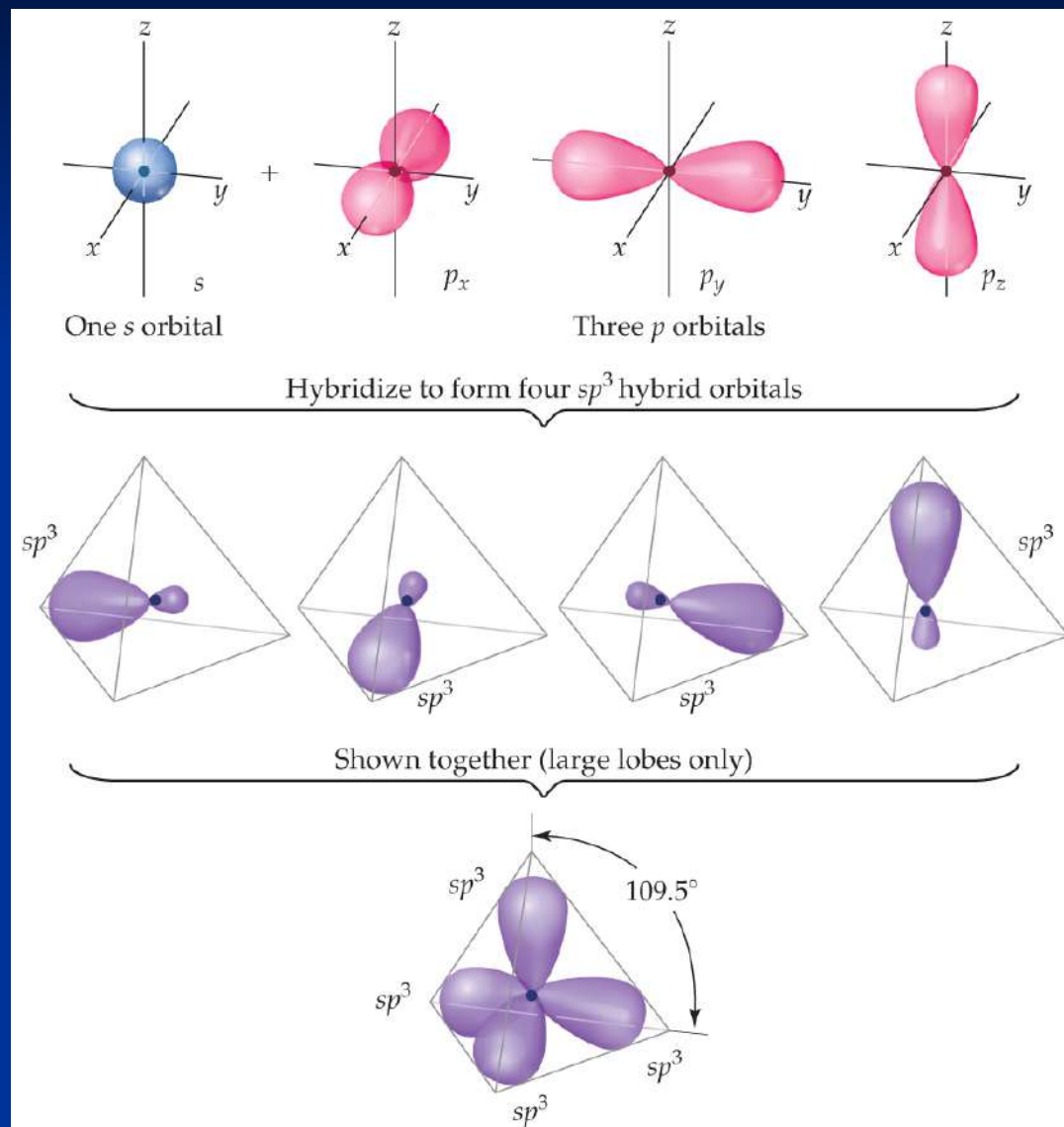


In an sp^2 hybridized atom, we saw that there was one unhybridized $2p$ orbital. How many unhybridized $2p$ orbitals remain on an atom that has sp^3 hybrid orbitals?

- a. One
- b. Two
- c. Three
- d. None

Carbon: sp^3 Hybridization

With carbon, we get four degenerate sp^3 orbitals.

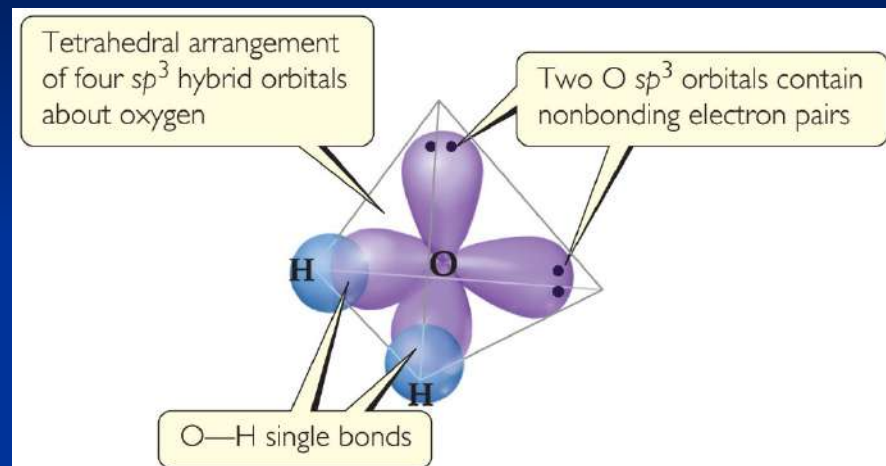


Hypervalent Molecules

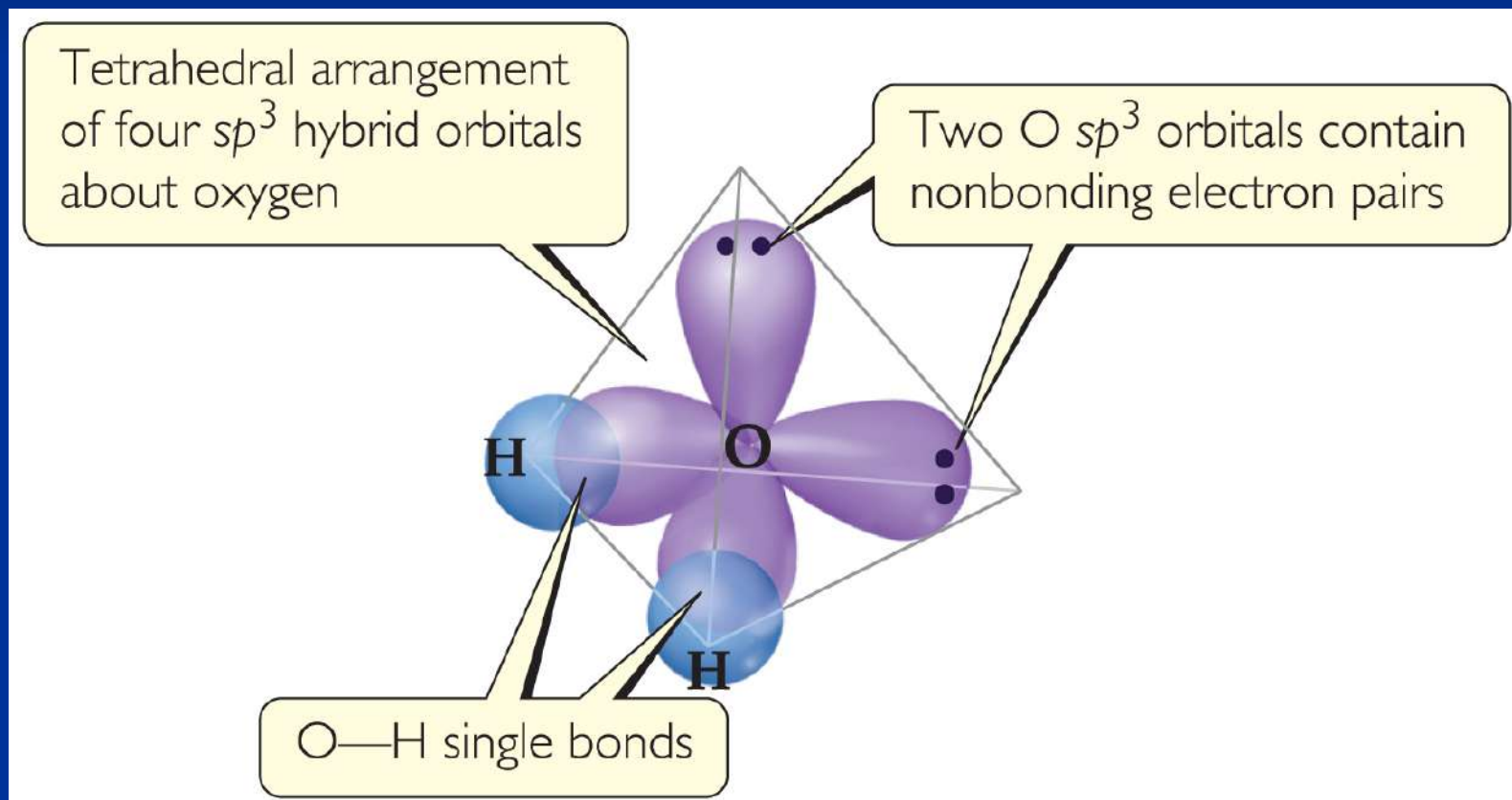
- The elements which have *more* than an octet
- Valence-Bond model would use *d* orbitals to make more than four bonds.
- This view works for period 3 and below.
- Theoretical studies suggest that the energy needed would be too great for this.
- A more detailed bonding view is needed than we will use in this course.

What Happens with Water?

- We started this discussion with H_2O and the angle question: Why is it 104.5° instead of 90° ?
- Oxygen has two bonds and two lone pairs—four electron domains.
- The result is sp^3 hybridization!



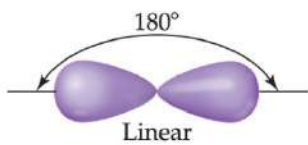
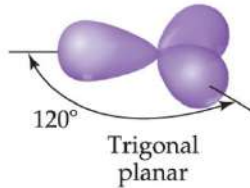
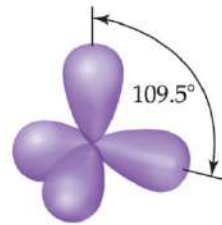
Does it matter which of the two sp^3 hybrid orbitals are used to hold the two nonbonding electron pairs?



Hybrid Orbital Summary

- 1) Draw the Lewis structure.
- 2) Use VSEPR to determine the electron-domain geometry.
- 3) Specify the hybrid orbitals needed to accommodate these electron pairs.

Table 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p	Two sp	 Linear	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	 Trigonal planar	BF_3, SO_3
s, p, p, p	Four sp^3	 Tetrahedral	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

Sample Exercise 9.5

■ 1) Indicate the hybridization of orbitals employed by the central atom in:

■ A) NH_2^-

■ 2) Predict the electron-domain geometry and the hybridization of the central atom in:

■ A) SO_3^{2-}

Practice Exercise 1

For which of the following molecules or ions does the following description apply? “The bonding can be explained using a set of sp^2 hybrid orbitals on the central atom, with one of the hybrid orbitals holding a nonbonding pair of electrons.”



(e) More than one of the above

9.6 Multiple Bonds

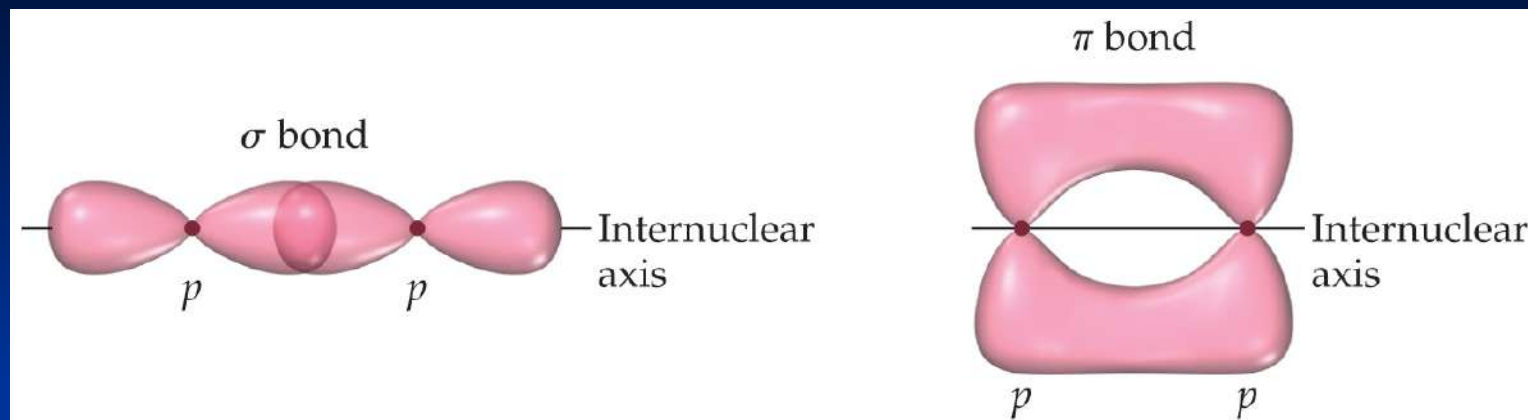
Bond Order

- Single bond = 1
- Double bond = 2
- Triple bond = 3
- If there is resonance, bond order is a fraction
 - Ex: ozone is $3/2$ (three total bonds for two locations)
 - Ex: nitrate ion is $4/3$ (four total bonds for three locations)

Types of Bonds

- How does a double or triple bond form?
- It *can't*, if we only use hybridized orbitals.
- *However*, if we use the orbitals which are *not* hybridized, we can have a “side-ways” overlap.
- Two types of bonds:
 - Sigma (σ) bond
 - Pi (π) bond

Sigma (σ) and Pi (π) Bonds

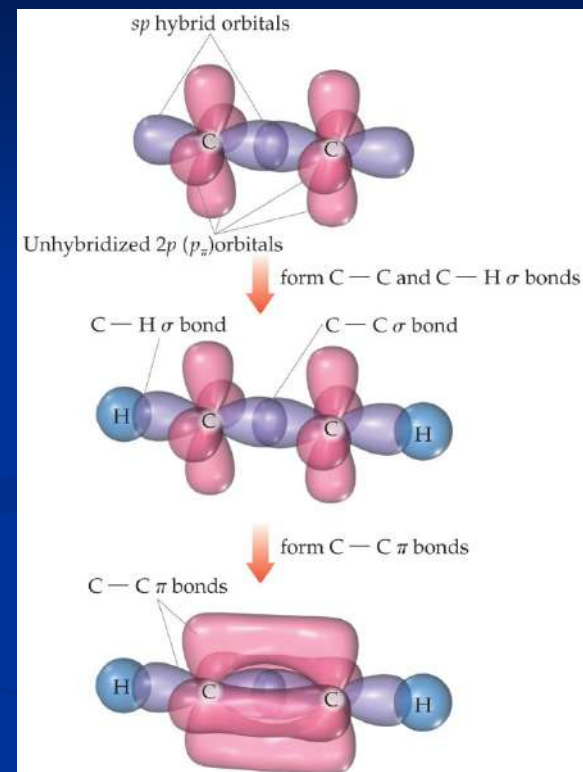
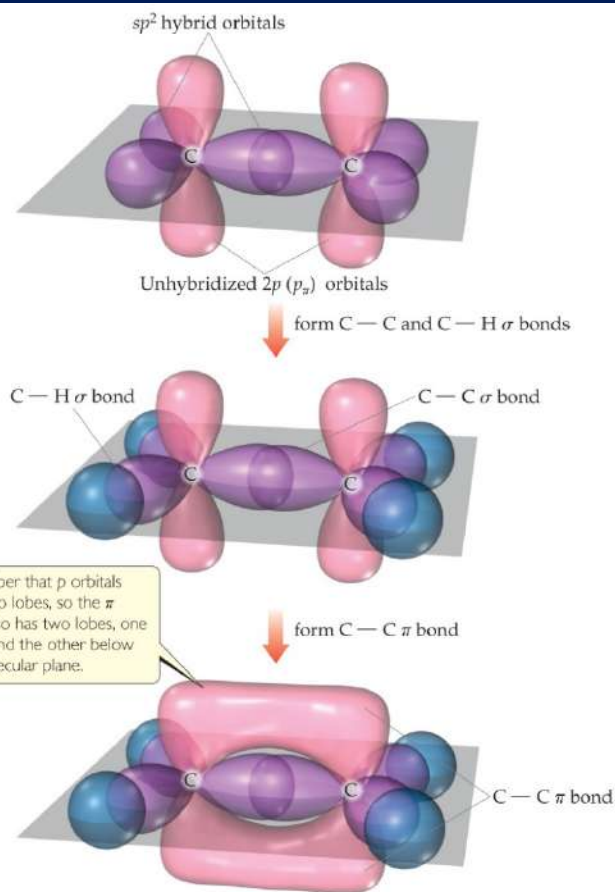


- Sigma bonds are characterized by
 - head-to-head overlap.
 - cylindrical symmetry of electron density about the internuclear axis.
- Pi bonds are characterized by
 - side-to-side overlap.
 - electron density above and below the internuclear axis.

Bonding in Molecules

■ Single bonds are always σ -bonds.

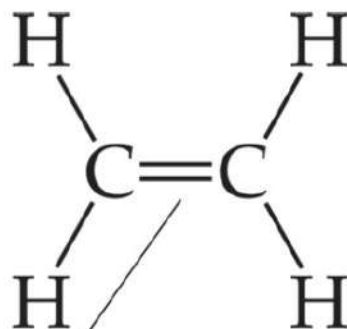
■ Multiple bonds have one σ -bond, all other bonds are π -bonds.



Multiple Bonds



One σ bond



One σ bond plus
one π bond



One σ bond plus
two π bonds

The molecule called *diazine* has the formula N_2H_2 and the Lewis structure

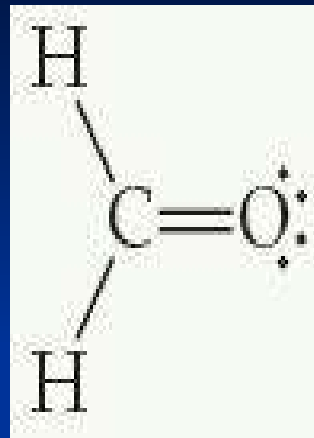


Do you expect diazine to be a linear molecule?
If not, do you expect the molecule to be planar?

- The molecule is both linear and planar.
- The molecule is not linear, but is planar.
- The molecule is linear, but not planar.
- The molecule is neither linear nor planar.

Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlaps of appropriate hybridized and unhybridized orbitals.

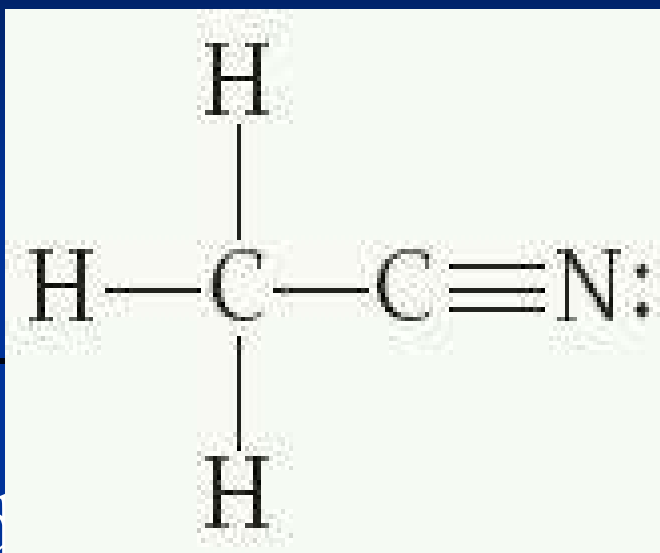
Practice Exercise 1

We have just arrived at a bonding description for the formaldehyde molecule. Which of the following statements about the molecule is or are true?

- (i) Two of the electrons in the molecule are used to make the π bond in the molecule.
 - (ii) Six of the electrons in the molecule are used to make the σ bonds in the molecule.
 - (iii) The C—O bond length in formaldehyde should be shorter than that in methanol, H_3COH .
- (a) Only one of the statements is true.
 - (b) Statements (i) and (ii) are true.
 - (c) Statements (i) and (iii) are true.
 - (d) Statements (ii) and (iii) are true.
 - (e) All three statements are true.

Practice Exercise 2

Consider the acetonitrile molecule:



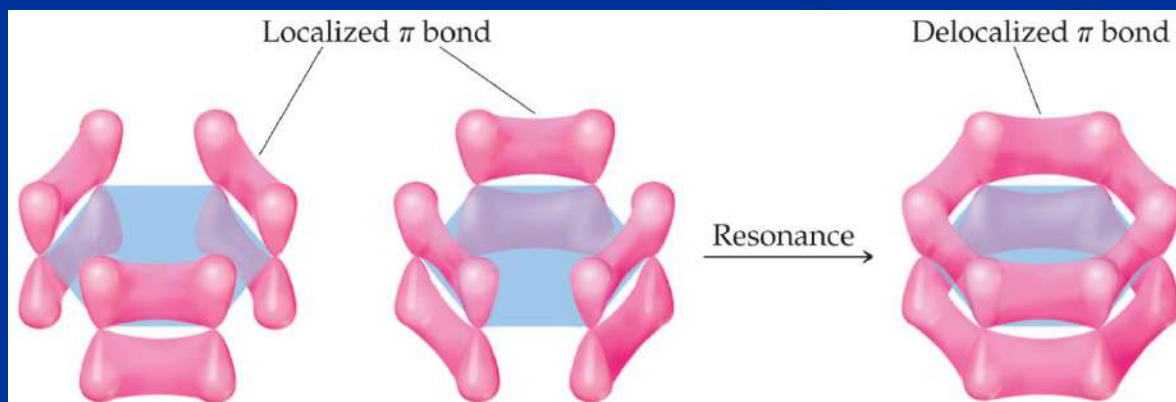
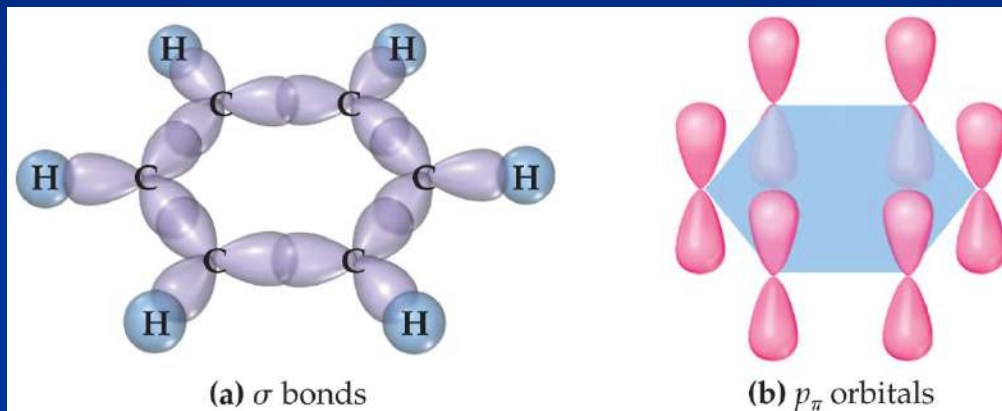
(a) Predict the hybridization around each carbon atom; (b) determine the hybridization at each of the carbon atoms; (c) determine the total number of sigma and pi bonds in the molecule.

Localized or Delocalized Electrons

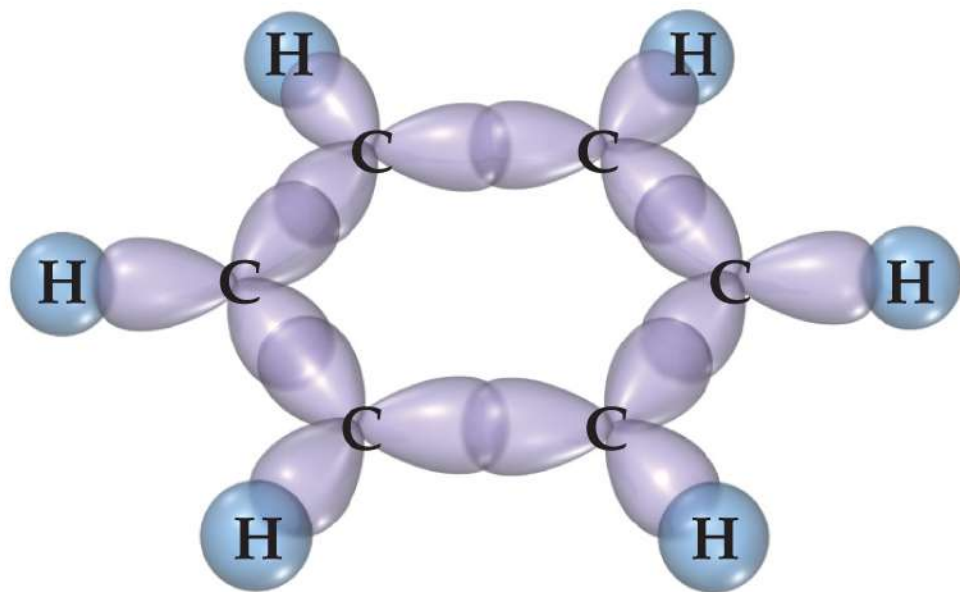
- Bonding electrons (σ or π) that are specifically shared between two atoms are called **localized** electrons.
- In many molecules, we can't describe all electrons that way (resonance); the other electrons (shared by multiple atoms) are called **delocalized** electrons.

Benzene

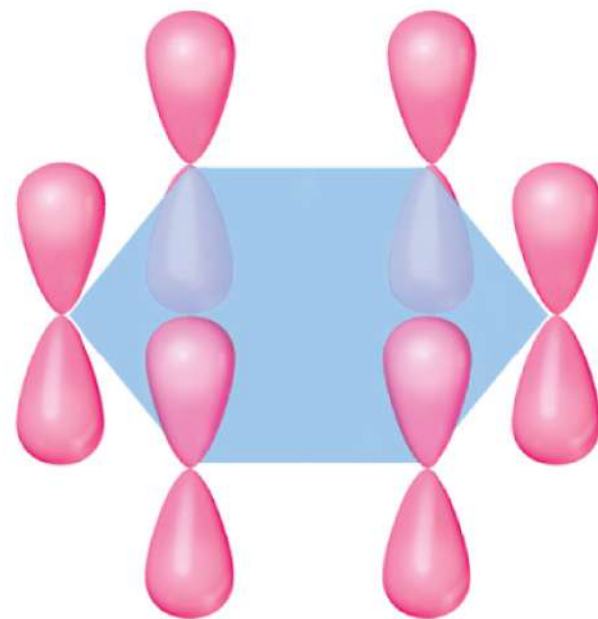
The organic molecule benzene (C_6H_6) has six σ -bonds and a p orbital on each C atom, which form delocalized bonds using one electron from each p orbital.



What are the two kinds of σ bonds found in benzene?



(a) σ bonds



(b) p_π orbitals

Sample Exercise 9.7 Delocalized Bonding

Describe the bonding in the nitrate ion, NO_3^- . Does this ion have delocalized π bonds?

Practice Exercise 2

- Which of the following molecules or ions will exhibit delocalized bonding: SO_2 , SO_3 , SO_3^{2-} , H_2CO , and NH_4^+ ?

Sample Integrative Exercise

Elemental sulfur is a yellow solid that consists of S_8 molecules. The structure of the S_8 molecule is a puckered, eight-membered ring. Heating elemental sulfur to high temperatures produces gaseous S_2 molecules: $S_8(s) \rightarrow 4 S_2(g)$

- (a) The electron configuration of which period 2 element is most similar to that of sulfur?
- (b) Use the VSEPR model to predict the S—S—S bond angles in S_8 and the hybridization at S in S_8 .
- (c) Use average bond enthalpies (Table 8.4) to estimate the enthalpy change for this reaction. Is the reaction exothermic or endothermic?