



**AP<sup>®</sup> Chemistry**  
**Curriculum Module:**  
Chemical Bonding

2010  
**Curriculum Module**

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# I. Introduction

Arden P. Zipp

This AP® Chemistry Curriculum Module will address several aspects of chemical bonding, which include:

- Writing and using Lewis structures
- Predicting molecular shapes with the valence shell electron pair repulsion (VSEPR) theory
- Describing molecules and orbitals with the valence bond (VB) theory
- Predicting the polarity of bonds and molecules
- Describing the types and effects of intermolecular forces

Each of these topics covers material that has been examined on past AP Chemistry Exams and, no doubt, will be on future ones. Individuals with a great deal of experience with AP Chemistry, including teachers, readers, members of the AP Chemistry Development Committee and contributors to previous resources for this course, wrote the selections.

Before exploring the topics mentioned above, it should be remembered that chemistry is based on experiment, and even the most abstract aspects of chemical bonding have been developed to account for behavior observed in nature. This behavior includes the structures of individual molecules and the forces between them.

Information about the structures of molecules can be gathered by a variety of spectroscopic methods, especially infrared (IR) spectroscopy; by diffraction methods; or by measurements of dipole moments. IR spectra can provide insight into the strengths of bonds between atoms, since the frequencies of IR vibrations increase with bond strength (but also depend on atomic masses). Diffraction methods, of which X-ray diffraction is the most common, can determine the positions of atoms within molecules. Atomic positions yield conclusions about bond lengths (and bond strengths, which are inversely related to bond lengths) as well as about bond angles. Dipole moment measurements can be used to draw conclusions about the polarity of molecules and the distribution of electrons and/or the arrangement of atoms within them. A relatively new technique called photoelectron spectroscopy (PES) can actually provide information about the energies of electrons within molecules.

Conclusions about the forces between molecules are usually obtained from a consideration of the physical properties they exhibit in bulk, such as melting points, boiling points, vapor pressures and enthalpy changes associated with these phenomena. Melting points, boiling points and enthalpy changes increase with an increase in intermolecular forces, while the vapor pressure decreases.

The various sections of this curriculum module present the means to describe and/or predict different features of these experimental results. In the first essay, Adele Mouakad describes how Lewis structures can be used to obtain an estimate of the strengths of the bonds in molecules, since the strength of a bond increases with the number of electron pairs between the constituent atoms. In addition, Lewis structures also provide the basis for VSEPR structures, which offer the means to determine the bond angles of both neutral and ionic species, as set forth in the second essay. The valence bond theory offers an alternate means to determine bond angles (through the geometries of atomic or hybrid orbitals) and bond lengths/strengths (via the formation of multiple bonds — sigma and pi); this is addressed in Marian DeWane's essay. In the fourth essay, David Hostage discusses the use of electronegativities to obtain bond polarities; and, along with molecular geometries, he outlines the application of these to establish the polarity of a molecule. In the final essay, Valerie Ferguson describes dispersion forces, dipole-dipole interactions and hydrogen bonds, along with their origins and their relative strengths.

The authors hope you enjoy reading these selections and find them useful.

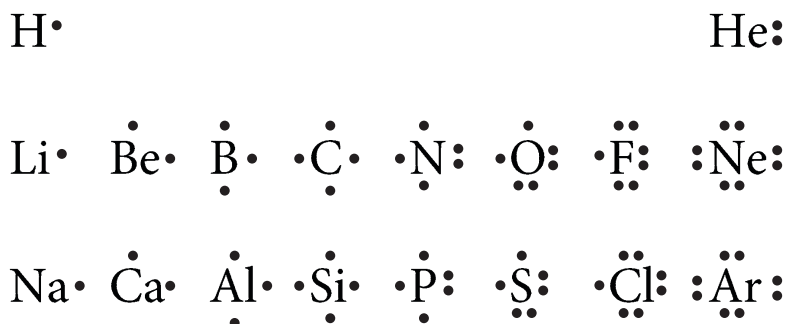
## II. Lewis Structures

Adele Mouakad

### Introduction

In 1916, Gilbert N. Lewis, one of the most famous American chemists, formulated the idea that a covalent bond consisted of a shared pair of electrons. His ideas on chemical bonding were expanded upon by Irving Langmuir and became the inspiration for the studies on the nature of the chemical bond by Linus Pauling. Lewis used dots to represent the valence electrons and introduced the concept that when atoms bonded they did so by pairing electrons. He also suggested that one of the driving forces of chemical bonding was the acquisition of eight electrons by each atom in analogy with the very stable noble gases. This is referred to as the octet rule, which is the guiding principle when writing Lewis (electron dot) structures. Although the structures of molecules as written do not imply a sense of the shape of the molecule or ion considered, they can be used in conjunction with the VSEPR theory (described in the next essay in this volume) to determine shapes.

The Lewis dot structures for molecules are developed from those of individual atoms and are given for atoms of the elements in the first four periods (excluding the transition elements) in the graphic below.



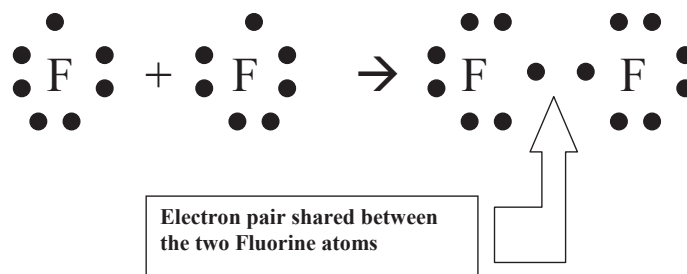
The structures are written to show the number of electrons present in the highest energy shell (valence) rather than the actual electron configurations in the free atoms. (For example, the two electrons in Be are actually paired, as are two of the three in B and two of the four in C.) All the elements in a given group or family have the same Lewis dot structure because they all have the same number of valence electrons.

Lewis structures are used to represent molecules. The covalent bond in the hydrogen molecule,  $\text{H}_2$ , can be represented as follows:



This is called a single covalent bond; a pair of electrons is shared between the two hydrogen atoms. The dash is also used to represent a pair of bonding electrons. Hydrogen cannot follow the octet rule, since it can have only two electrons after sharing, which is the configuration of helium. In some textbooks, this is referred to as the duet rule.

In a similar fashion, two fluorine atoms can pair electrons to form an  $F_2$  molecule.



A line or pair of dots between two atoms represents a bonding pair of electrons, while a pair of dots on the periphery of a molecule is referred to as a nonbonding or lone pair.

## Multiple Bonding

Some molecules require more than single bonds to provide each atom with the required octet. Examples include the oxygen molecule  $O_2$  (12 valence electrons), which requires a double bond.



Nitrogen ( $N_2$ ) requires a triple bond between the two nitrogen atoms to provide each nitrogen with an octet of electrons.



Multiple bonds are formed primarily by the carbon, nitrogen and oxygen atoms.

The rules below can be used to develop Lewis structures for more complex species.

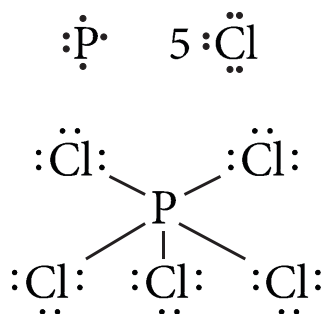
## Rules for Writing Lewis Structures

- Decide on the sequence of atoms.
  - For  $AB_n$  formulas, the single atom usually is the central atom in the molecule (e.g., in  $CH_4$ ,  $NH_3$  and  $H_2O$ , the central atoms are C, N and O, respectively). H and F are *never* central and other halogens seldom are.
  - Compounds with symmetrical formulas often adopt corresponding structures (e.g., the atomic arrangement in  $H_2O_2$  is H-O-O-H).





electrons to form species such as  $\text{PCl}_3$ , but it can also use all five electrons to form molecules like  $\text{PCl}_5$ , in which there are 10 electrons around the P.

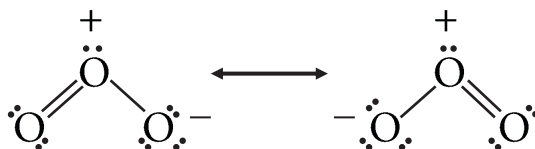


Many other molecules contain central atoms with more than an octet of electrons. The list includes compounds of sulfur, selenium, tellurium, the halogens (except for fluorine) and the noble gases: krypton, xenon and radon.

## Resonance

Some molecules can be represented by more than one Lewis dot structure. Two (or more) different Lewis dot structures for a given species are called *resonance structures* or *resonance forms*. It is important to understand that these resonance forms do not actually exist, even briefly, but are simply the best approximations to the actual molecular structure that can be made within the constraints of the Lewis theory. Resonance forms are useful, however, because the structure of a molecule described by resonance is intermediate between the structures of its resonance forms. For such molecules, the various resonance forms are typically written as connected by double-headed arrows to show their relationship.

Ozone, a high energy allotrope of oxygen with the formula  $\text{O}_3$ , provides a good example of resonance. In order to provide each of the three oxygen atoms in ozone (18 electrons) with an octet of electrons (as required by the Lewis theory), two of the oxygen atoms must be connected by a single bond and the other by a double bond. There are, however, two different ways this can be done, depending on where the double bond is placed, as shown in the diagram below.



Experiments indicate that the two bonds in the  $\text{O}_3$  molecule do not have different properties, as they would if the single and double bonds were fixed in position. Rather, the two bonds are equivalent with properties intermediate between those of a single and a double bond.

Carbon dioxide,  $\text{CO}_2$ , is another molecule for which a number of resonance forms can be written. First, there is the most familiar form of  $\text{CO}_2$  in which the two oxygen atoms are bonded to the carbon by two double bonds. In addition, two other resonance forms can be written, each containing a single and a triple bond.

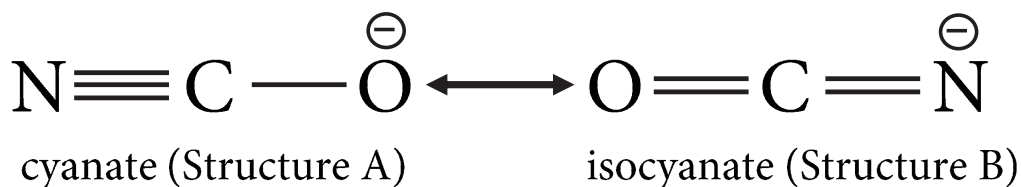
Other familiar examples of species that are best described by resonance include the carbonate ( $\text{CO}_3^{2-}$ ) and the nitrate ( $\text{NO}_3^-$ ) ions, each of which contains 24 valence electrons with the lone atom at the center of the ion. Three equivalent resonance forms with a double bond and two single bonds can represent each species. As discussed above, the actual structure of each of these ions is intermediate between the extremes represented by the resonance forms.

## Formal Charge

Formal charge represents the difference between the number of valence electrons an atom possesses in its free state and the number assigned to it in a given Lewis structure. The number of valence electrons assigned to an atom in the bonded state can be found by counting all of the electrons belonging exclusively to that atom (i.e., nonbonding electrons) and one-half of the electrons in the bonds to it. The formal charge is obtained by subtracting the number obtained in this way from the number in the free atom. This is summarized in the following equation:

$$\text{Formal charge} = \text{Number of valence electrons originally} - \left[ \begin{array}{l} \text{nonbonding} \\ \text{electrons} \end{array} + \frac{1}{2} \begin{array}{l} \text{bonding} \\ \text{electrons} \end{array} \right]$$

The formal charge concept is a useful one because it may be helpful in determining the relative stabilities of several resonance forms or even in establishing the best arrangement of atoms in molecules for which a central atom is not immediately apparent. The cyanate ion,  $\text{NCO}^-$ , with two reasonable resonance forms (labeled a = cyanate and b = isocyanate) provides a useful example.



The formal charge for each of the atoms in structure (a) would be:

$$\text{FC: N} = 5 e^- - [2 \text{ nonbond } e^- + \frac{1}{2} (6 \text{ bond } e^-)] = \text{N} = 5 - 5 = -0$$

$$\text{FC: C} = 4 e^- - [ \frac{1}{2} (8 \text{ bond } e^-) ] = \text{C} = 4 - 4 = 0$$

$$\text{FC: O} = 6 e^- - [6 \text{ nonbond } e^- + \frac{1}{2} (2 \text{ bond } e^-)] = \text{O} = 6 - 7 = -1$$

Similarly, the formal charge for each of the atoms in structure (b) would be:

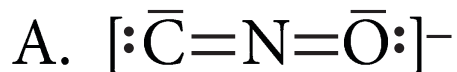
$$\text{FC: N} = 5 e^- - [4 \text{ nonbond } e^- + \frac{1}{2} (4 \text{ bond } e^-)] = \text{N} = 5 - 6 = -1$$

$$\text{FC: C} = 4 e^- - [\frac{1}{2} (8 \text{ bond } e^-)] = \text{C} = 4 - 4 = 0$$

$$\text{FC: O} = 6 e^- - [4 \text{ nonbond } e^- + \frac{1}{2} (4 \text{ bond } e^-)] = \text{O} = 6 - 6 = 0$$

Structure A (Cyanate Ion) would be more stable than Structure B (Isocyanate Ion) because the formal charges have been minimized at 0, 0 and -1. However, Structure A (Cyanate Ion) is also more stable than Structure B (Isocyanate Ion) because the -1 formal charge is located on O, which has a greater attraction for electrons than the N.

Now examine the unstable fulminate ion:



The fulminate ion has a similar molecular formula to the cyanate ion even though its structural formula is different. When it is analyzed in terms of formal charge, a determination as to why it is unstable can be made.

For Structure A (Cyanate Ion):

$$\text{FC: N} = 5 e^- - [0 \text{ nonbond } e^- + \frac{1}{2} (8 \text{ bond } e^-)] = 5 - 4 = +1$$

$$\text{FC: C} = 4 - [4 \text{ bond } e^- + \frac{1}{2} (4 \text{ bond } e^-)] = 4 - 6 = -2$$

$$\text{FC: O} = 6 - [4 \text{ non } e^- + \frac{1}{2} (4 \text{ bond } e^-)] = 6 - 6 = 0$$

The formal charges are N +1, C -2 and O 0, with nitrogen having a +1 charge and carbon a -2 charge. In this case the charges are not a minimum and carbon, the least electronegative of the three atoms, has formal charge of -2. In the cyanate ion the formal charges are 0, 0 and -1, with oxygen, the most electronegative atom of the three, being the -1.

In evaluating the stabilities of resonance forms, the following rules apply: (1) minimize nonzero formal charges; (2) avoid nonzero formal charges on adjacent atoms; and (3) place negative formal charges on atoms with greater electron attractions and positive formal charges on atoms with lower electron attractions.

Determine the formal charges on the atoms in the hypothetical species with the atomic arrangement  $\text{CON}^-$  and use these to explain why this ion is unknown. The reader should discover using the same electron arrangements as in structures (a), (b) and (c), the formal charges are (a) C -2, O +2, N -1; (b) C -3, O +1, N +1; (c) C 0, O +1, N -2. All three resonance forms have formal charges, with positive formal charges on the O atom.

## Conclusion

Based on the ideas described in the discussion above, the reader should be able to:

- Write Lewis electron dot structures for a variety of molecules
- Describe the bonds in those structures as single, double or triple bonds
- Write and discuss resonance forms where appropriate
- Determine formal charges for atoms within molecules and ions
- Use formal charges to predict the relative stabilities for several resonance forms

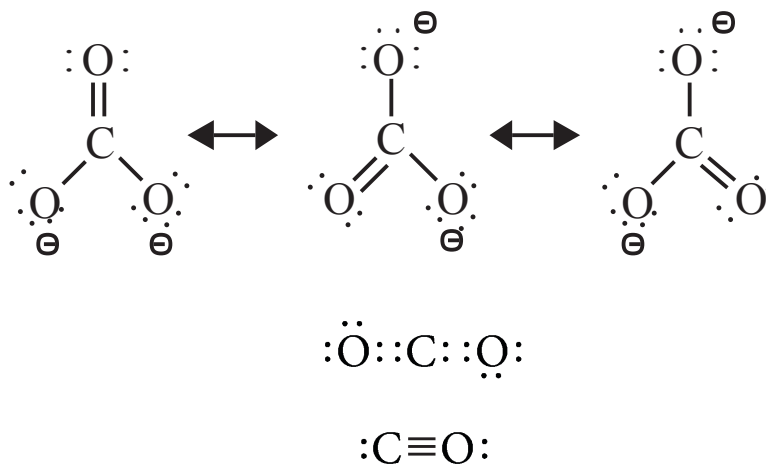
## Sample Questions from AP<sup>®</sup> Chemistry Examinations

### 1982 D

- Draw the Lewis electron-dot structures for  $\text{CO}_3^{2-}$ ,  $\text{CO}^2$  and  $\text{CO}$ , including resonance structures where appropriate.
- Which of the three species has the shortest C-O bond length? Explain the reason for your answer.
- Account for the fact that the carbon-oxygen bond length in  $\text{CO}_3^{2-}$  is greater than the carbon-oxygen bond length in  $\text{CO}^2$ .

Answers:

(a)



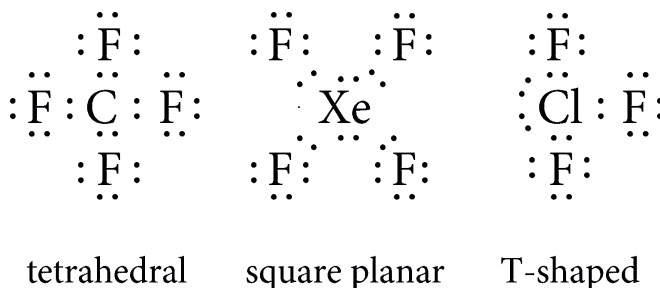
- (b) CO has the shortest bond because there is a triple bond, or because the bond order is 3, meaning it has the greatest number of shared electrons between the carbon and the oxygen atom.
- (c) The carbonate ion exhibits resonance. Therefore, due to the delocalized electrons, the C-O bond is intermediate in size between a single bond and a double bond; whereas in carbon dioxide, the carbon-oxygen bond is a double bond.

**1989 D**

- (a) Draw a Lewis electron-dot structure for each of the molecules above and identify the shape of each.

*Answer:*

(a)

**1990 D**

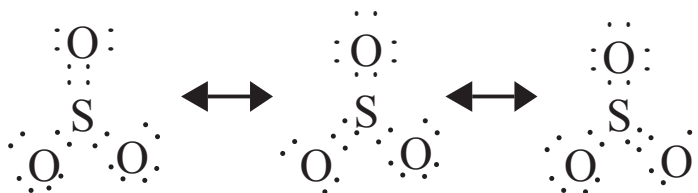
Use simple structure and bonding models to account for each of the following:

- (a) The bond length between the two carbon atoms is shorter in  $\text{C}_2\text{H}_4$  than in  $\text{C}_2\text{H}_6$ .
- (b) All the bond lengths in  $\text{SO}_3$  are identical and are shorter than a sulfur-oxygen single bond.

*Answers:*

- (a)  $\text{C}_2\text{H}_6$  has only single bonds.  $\text{C}_2\text{H}_4$  has a double bond between the two carbon atoms. The more electrons that are involved in bonding, the shorter the bond length will be.

(b)



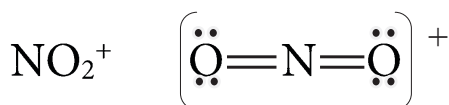
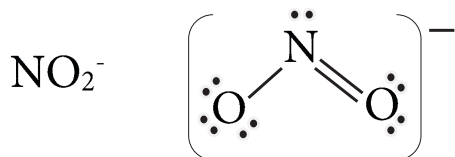
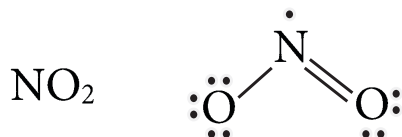
SO<sub>3</sub> exhibits resonance. Due to the delocalized electrons, the electrons in the resonance structures are distributed evenly between the sulfur and oxygen atoms. Due to this, there is only one form of the SO<sub>3</sub> molecule, and the bond lengths between the oxygen and the sulfur are intermediate between characteristic single- and double- bond lengths.

**1992 D**

Nitrogen is the central atom in each of the species given above.

(a) Draw the Lewis electron-dot structure for each of the three species.

*Answer:*

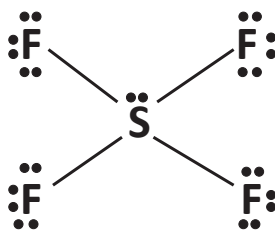
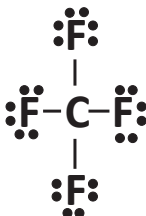


**1999 D**

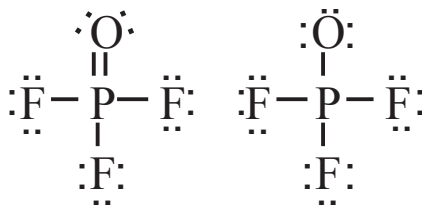
Answer the following question using principles of chemical bonding and molecular structure.

(b) Consider the molecules  $\text{CF}_4$  and  $\text{SF}_4$ .

Draw the complete Lewis electron-dot structure for each molecule.

**2005 D**

(c) Two Lewis structures can be drawn for the  $\text{OPF}_3$  molecule, as shown below.

**Structure 1****Structure 2**

- How many sigma bonds and how many pi bonds are in Structure 1?
- Which one of the two structures best represents a molecule of  $\text{OPF}_3$ ? Justify your answer in terms of formal charge.

*Answers:*

- One  $\Psi$  bond and four  $\sigma$  bonds
- Structure 1. In Structure 1, oxygen has a formal charge of 0 (six valence electrons – six assigned electrons), each fluorine is 0 (seven valence electrons – seven assigned electrons), and phosphorus is 0 (five valence electrons – five assigned electrons).

In Structure 2, oxygen has a formal charge of  $-1$  (six valence electrons  $-$  seven assigned electrons), each fluorine is  $0$  (seven valence electrons  $-$  seven assigned electrons), and phosphorus is  $+1$  (five valence electrons  $-$  four assigned electrons). Structures where all the atoms have formal charges of  $0$  are preferred.



# III. Valence Shell Electron Pair Repulsion Theory

Arden P. Zipp

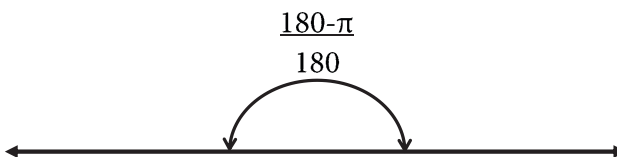
The valence shell electron pair repulsion (VSEPR) theory was developed as a way to predict molecular geometries (based on electron dot structures) without invoking the geometry or hybridization of orbitals. The basic principle of the VSEPR theory is that electrons repel one another because of their like (negative) charges and that the shapes of covalently bonded species can be determined by the repulsion of electrons (either bonding or nonbonding). This theory offers the simplest means available to account for (or to predict) the structures of molecules and ions, which can be divided into two categories. These categories include species in which:

- Only bonding electrons surround the central atom.
- The central atom is surrounded by both bonding and nonbonding electrons.

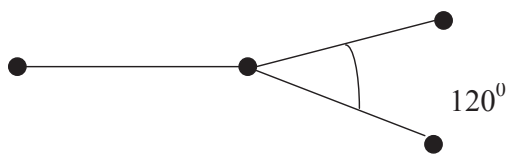
Species in the former category are designated as AX<sub>n</sub> species in many textbooks, where A represents the central atom, X represents the atoms or groups surrounding it, and n represents the number of such groups. The geometries of such species are often referred to as “ideal” because the positions of the surrounding substituents (atoms or groups) are not perturbed by the presence of nonbonding electrons. The effect of nonbonding electrons is discussed below. As a first approximation, the sizes of the atoms and the number of bonds (e.g., single, double or triple) have little effect on the geometry.

## Ideal Geometries

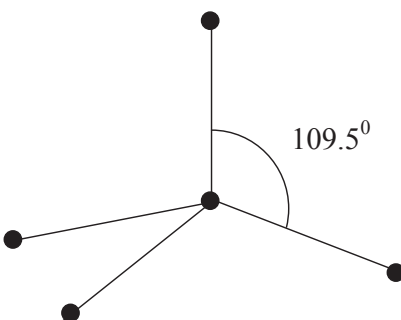
Two bonding pairs: These will be the farthest away from one another when they are on opposite sides of the central atom to give a linear species with a 180° angle between the bonds.



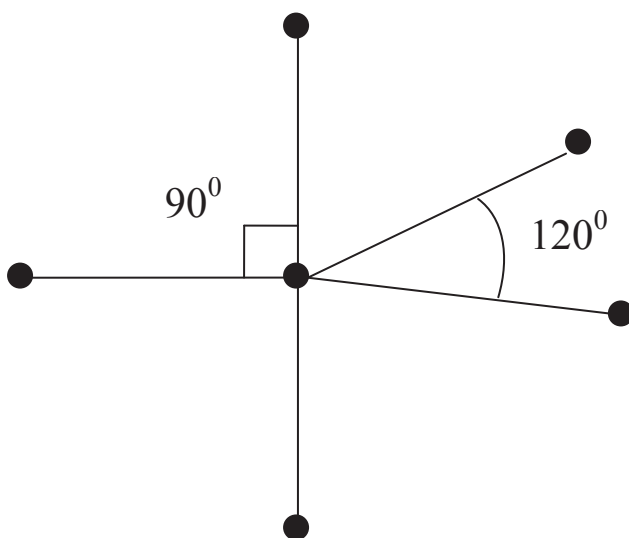
Three bonding pairs: Repulsion will be minimized with the three pairs at the corners of an equilateral triangle with angles of  $120^\circ$ .



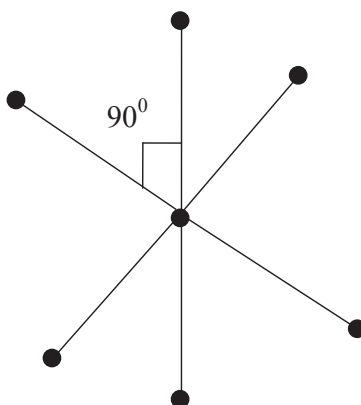
Four bonding pairs: Although four pairs would form a square if constrained to one plane, the interaction among them is decreased if two pairs rotate out of the plane to form a three-dimensional shape called a tetrahedron. Every bond angle in this species is  $109.5^\circ$ .



Five bonding pairs: In this species the five electron pairs are not equivalent, even though they are all bonding pairs. The lowest energy configuration has three pairs in an equilateral triangle (designated as the equatorial plane), with the other two at  $90^\circ$  above and below the plane of the triangle (axial). There are two different bond angles:  $120^\circ$  for the equatorial groups and  $90^\circ$  for the axial substituents (relative to the equatorial ones).



Six bonding pairs: Pairs will be found at the corners of an eight-sided geometric figure called an octahedron, with the angles between adjacent pairs of  $90^\circ$ .



A summary of these results is presented in the table below.

Formulas, Geometries, Bond Angles and Example Species for  $AX_2 - AX_6$

Formula	Location of $e^-$ pairs	Bond Angles	Example
$AX_2$	linear	$180^\circ$	$BeH_2$
$AX_3$	triangular	$120^\circ$	$BH_3$
$AX_4$	tetrahedral	$109.5^\circ$	$CH_4$
$AX_5$	trigonal	$90^\circ$	$PCl_5$
	bipyramidal	$120^\circ$	
$AX_6$	octahedral	$90^\circ$	$SF_6$

## Teaching Tips

- Tying off inflated balloons and twisting the tails together can demonstrate the fact that these shapes occur as a result of repulsion. (Note: Six balloons are often too cumbersome to allow their attachment in this way.)
- The first four shapes can be illustrated with a “personal” approach by using the hands to represent two bonding pairs on opposite sides of the body (which represent the central atom), by using the hands together and the feet spread for three pairs, and by using both hands extended and both feet extended for four pairs.
- You can portray the advantage of the tetrahedron over the square by using a piece of clothesline. The length of the clothesline required with the ends in one’s hands and the middle under the feet will be less when the feet are under the shoulders (“square”) than with the hands twisted in front and behind the head (“tetrahedron”).

Because the spatial relationships of molecules are best appreciated by examining them in three dimensions, a hands-on activity using sets of molecular models is suggested.

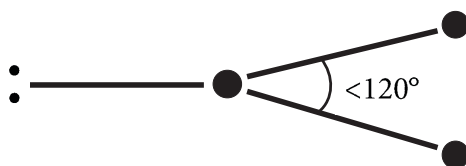
## Effect of Nonbonded Electrons

When a molecule contains nonbonding as well as bonding electrons around the central atom, it is necessary to distinguish between the geometries of the electrons and those of the groups of atoms around the central atom (referred to as the molecular geometry). In these cases, the geometries of the bonded atoms will obviously differ from those found in species that contain an equal number of bonding electrons. Chemists are usually interested in the positions of the atoms, which can be determined experimentally. The positions of the nonbonding electrons are usually assigned by deduction from the location of the atoms surrounding the central atom.

The molecular geometry of a species that contains nonbonding as well as bonding electrons can be determined by starting with the ideal geometry of the corresponding species with the same total number of electrons. The geometry will differ from the ideal one by the absence of one or more substituents. In addition, the bond angle(s) between the remaining bonded atoms will be less than the ideal angle(s) due to the greater repulsion of the nonbonding electrons. (See below.)

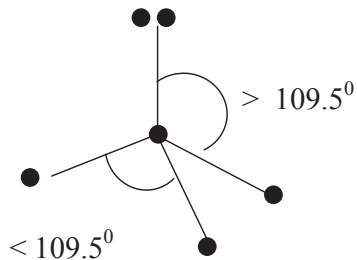
### Structures based on AX<sub>3</sub>

Two bonding pairs, one nonbonding pair: If one of the electron pairs in such a species is nonbonding, the molecule is described as bent, with an angle between the two bonded pairs that is less than 120°.

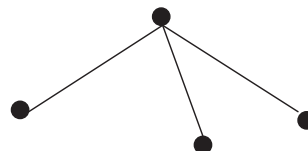


## Structures based on AX<sub>4</sub>

Three bonding pairs, one nonbonding pair: When one of the electron pairs is nonbonding, the central atom and the three bonded atoms describe a triangular (trigonal) pyramid.

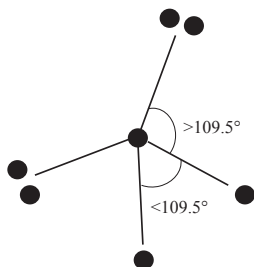


**Atoms and  
nonbonding pair**

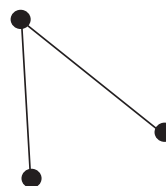


**Atoms only  
Trigonal Pyramid**

Two bonding pairs, two nonbonding pairs: Because the parent AX<sub>4</sub> species is nonplanar, this configuration can only lead to a bent geometry.



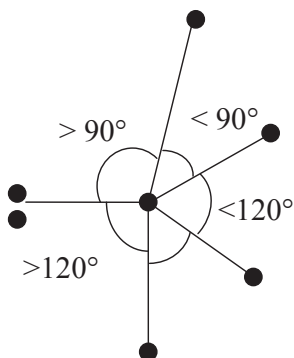
**Atoms and nonbonding pairs**



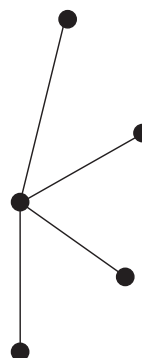
**Atoms only, bent**

## Structures based on AX<sub>5</sub>

Four bonding pairs, one nonbonding pair: Because the AX<sub>5</sub> species has nonequivalent pairs of electrons (axial and equatorial), a nonbonding pair (in place of a bonding pair) could assume different positions. Experiments indicate that the nonbonded pair is found in an equatorial position rather than an axial one. (This indicates that the repulsion between the lone pair, two bonding pairs at 120° and two others at 90° is less than that in the alternative structure with three bonding pairs at 90° and a bonding and nonbonding pair in axial positions.)

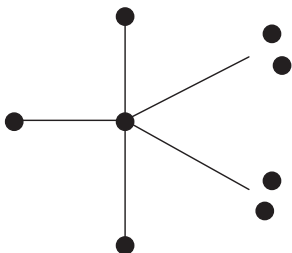


**Atoms and nonbonding pair**

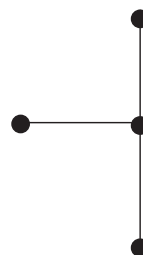


**Atoms only, seesaw**

Three bonding pairs, two nonbonding pairs: As above, the two nonbonding pairs occupy equatorial positions, leaving one equatorial and two axial positions for the bonding pairs, which gives the resulting species a T-shape.

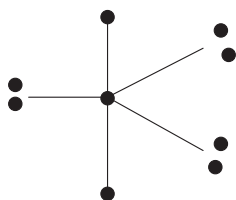


**Atoms and nonbonding pairs**



**Atoms only, T-shape**

Two bonding pairs, three nonbonding pairs: With three nonbonding pairs in the equatorial plane and the bonding pairs in axial positions, a species with such a formula will have a linear molecular geometry.



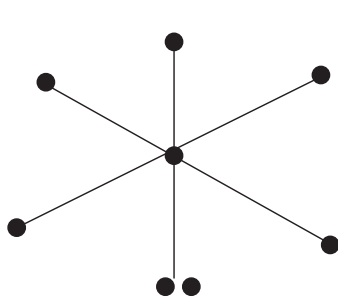
**Atoms and nonbonding pairs**



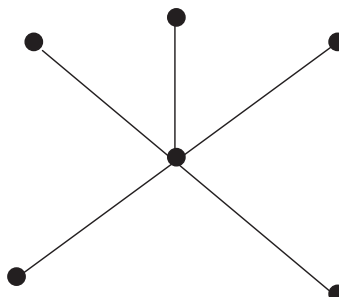
**Atoms only, linear**

## Structures based on AX<sub>6</sub>

Five bonding pairs, one nonbonding pair: Since all six positions of an octahedron are equivalent, replacing any of the six bonding pairs with a nonbonding pair will yield the same structure, referred to as a square pyramid.

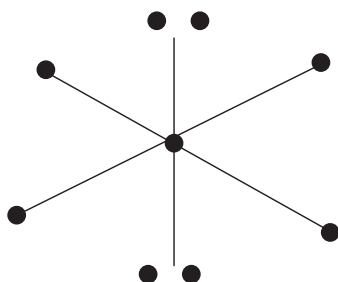


**Atoms and  
nonbonding pair**

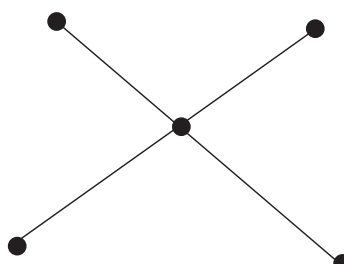


**Atoms only  
Square pyramid**

Four bonding pairs, two nonbonding pairs: When a second nonbonding pair is introduced to the square pyramid above, the repulsion between the nonbonding pairs will be minimized when they are opposite one another. This molecular geometry is square planar.



**Atoms and  
nonbonding pairs**



**Atoms only  
Linear**

As mentioned above, nonbonding electrons may decrease the angles between bonding electrons relative to those in ideal structures where all bonding electrons are equivalent (except for those in the trigonal bipyramid). This decrease can be understood on the grounds that bonding electron pairs are attracted by two positively charged nuclei, whereas nonbonding electrons are attracted to only one nucleus, allowing them to approach that nucleus more closely. As a consequence, the repulsion between nonbonding and bonding pairs of electrons is greater than that between bonding pairs. These results are summarized in the table below.

## Characteristics of Species Containing Both Bonding and Nonbonding Electron Pairs

Formula	Ideal Geometry	Bonding Pairs	Nonbonding pairs	Molecular Geometry	Bond Angle*	Example
$AX_2E$	trigonal planar	2	1	bent	$120^\circ$	$O_3$
$AX_3E$	tetrahedral	3	1	trigonal pyramidal	$<109.5^\circ$	$NH_3$
$AX_2E_2$	tetrahedral	2	2	bent	$<109.5^\circ$	$H_2O$
$AX_4E$	trigonal bipyramid	4	1	see-saw	$<90^\circ$ $<120^\circ$	$SF_4$
$AX_3E_2$	trigonal bipyramid	3	2	T-shaped	$90^\circ$	$ClF_3$
$AX_2E_3$	trigonal bipyramid	2	3	linear	$180^\circ$	$I_3^-$
$AX_5E$	octahedral	5	1	square pyramid	$90^\circ$	$ICl_5$
$AX_4E_2$	octahedral	4	2	square planar	$90^\circ$	$XeF_4$

[\* Nonbonding electrons reduce bond angle(s) from the ideal values, but the exact angles depend on the identity of the central and surrounding atoms. For example, the H-N-H angle in  $NH_3$  is  $107.5^\circ$ , but the F-N-F angle in  $NF_3$  is even smaller because the electronegative F atoms pull the bonding electrons further from the nitrogen. Similarly, the H-P-H angle in  $PH_3$  is less than the H-N-H angle because the bonding electrons between the P and H are farther from the P (because it is larger and less electronegative).]

## Teaching Tip

Many textbooks offer similar tables with formulas that specify the number of bonding and nonbonding pairs (e.g.,  $AX_3E$ ) and the corresponding molecular geometries. Although students may be tempted to memorize such tables, it is recommended that they learn only the ideal geometries and work out the nonideal ones as outlined above.



## Sample Questions from AP Chemistry Examinations

(NOTE: The answers below include explanations, but minimum acceptable responses are underlined.)

### 2004 Question 7

Use appropriate chemical principles to account for each of the following observations. In each part, your response *must* include specific information about *both* substances.

- (c) The shape of the  $\text{ICl}_4^-$  ion is square planar, whereas the shape of the  $\text{BF}_4^-$  ion is tetrahedral.

*Answer:* In the  $\text{ICl}_4^-$  ion, the iodine atom is surrounded by six pairs of electrons, four bonding pairs and two nonbonding pairs, so it will have a structure based on an octahedron. The two nonbonding pairs will occupy opposite corners (to minimize repulsion). The four bonding pairs will have a square planar geometry. The  $\text{BF}_4^-$  ion has four pairs of bonding electrons, so it will assume a tetrahedral geometry.

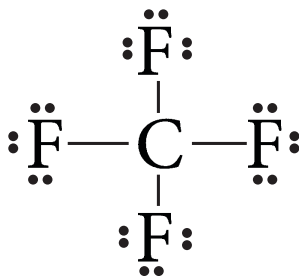
### 2005 Question 6

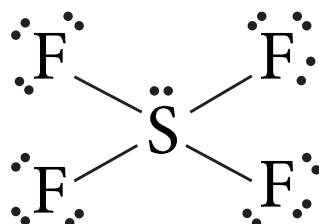
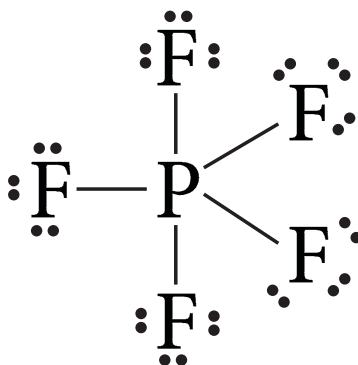
Answer the following questions that relate to chemical bonding.

- (a) In the boxes provided, draw the complete Lewis structure (electron-dot diagram) for each of the three molecules represented below.



*Answer:*





(Note: All electrons including nonbonding pairs must be shown!)

- (b) On the basis of the Lewis structures drawn above, answer the following questions about the particular molecule indicated.

- (i) What is the F-C-F bond angle in  $\text{CF}_4$ ?

*Answer:* The F-C-F angle is  $109.5^\circ$ . ( $\text{CF}_4$  has four bonding pairs of electrons and will be tetrahedral.)

- (iii) What is the geometric shape formed by the atoms in  $\text{SF}_4$ ?

*Answer:* Five pairs of electrons (four bonding pairs and one nonbonding pair) surround the S atom in SF. The electron pair shape will be trigonal bipyramid and the nonbonding pair will occupy one of the equatorial positions, making the geometry of the atoms a seesaw shape.

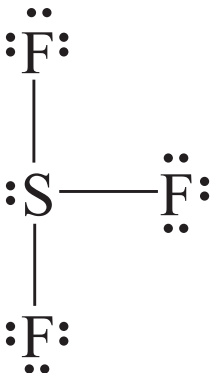
**2006 Question 7**

Answer the following questions about the structures that contain only sulfur and fluorine.

(a) The compounds  $\text{SF}_4$  and  $\text{BF}_3$  react to form an ionic compound according to the following equation:  $\text{SF}_4 + \text{BF}_3 \rightarrow \text{SF}_3\text{BF}_4$

(i) Draw a complete Lewis structure for the  $\text{SF}_3^+$  cation in  $\text{SF}_3\text{BF}_4$ .

*Answer:*



(iii) Identify the geometry of the  $\text{SF}_3^+$  cation that is consistent with the Lewis structure drawn in part (a)(i).

*Answer:* The  $\text{SF}_3^+$  ion has four pairs of electrons (three bonding pairs and a nonbonding pair). The structure is based on a tetrahedron. The nonbonding pair makes it trigonal pyramidal.

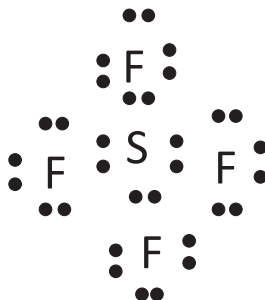
(iv) Predict whether the F-S-F bond angle in the  $\text{SF}_3^+$  cation is larger than, equal to, or smaller than  $109.5^\circ$ . Justify your answer.

*Answer:* The F-S-F angle will be less than  $109.5^\circ$  because the nonbonding pair will repel the bonding pairs more than they will repel one another.

(b) The compounds  $\text{SF}_4$  and  $\text{CsF}$  react to form an ionic compound according to the following equation:  $\text{SF}_4 + \text{CsF} \rightarrow \text{CsSF}_5$

(i) Draw a complete Lewis structure for the  $\text{SF}_5^-$  anion in  $\text{CsSF}_5$ .

*Answer:*



- (iii) Identify the geometry of the  $\text{SF}_5^-$  anion that is consistent with the Lewis structure drawn in part (b)(i).

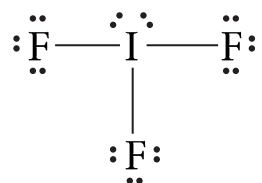
*Answer:* Six pairs of electrons (five bonding pairs and one nonbonding pair) surround the S atom. The electron geometry will be octahedral but the nonbonding pair will make the molecular geometry square pyramidal.

## 2007 Question 6

Answer the following questions that pertain to binary compounds.

- (a) In the box provided, draw a complete Lewis electron-dot diagram for the  $\text{IF}_3$  molecule.

*Answer:*



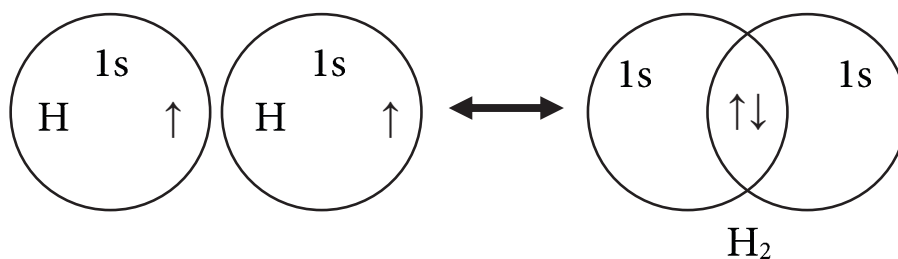
- (b) On the basis of the Lewis electron-dot diagram that you drew in part (a), predict the molecular geometry of the  $\text{IF}_3$  molecule.

*Answer:* There are five pairs of electrons (three bonding pairs and two nonbonding pairs) around the iodine atom. The electron pair geometry will be trigonal bipyramidal with the nonbonding pairs in the equatorial positions. The molecular geometry will be T-shaped.

## IV. Valence Bond Theory and the Hybridization Model

Marian DeWane

The valence bond theory was developed by Linus Pauling during the 1930s and is described in detail in his ground-breaking book, *The Nature of the Chemical Bond*<sup>1</sup>. The basic principle of the valence bond (VB) theory is that a covalent bond forms when an atomic orbital from one atom overlaps with an atomic orbital from another atom. The overlapping orbitals contain two electrons that have opposite spins in the ground state. A common example is an  $H_2$  molecule, which is formed when the s orbital of one H atom containing one electron overlaps with the s orbital of a second H atom. This is referred to as a *sigma bond*. Commonly, each atom in a sigma bond contributes one electron to the bond. In some instances, however, both electrons are contributed by one of the two atoms.



In the HF molecule, an H atom with the configuration  $1s^1$  is combining with an F whose configuration is  $1s^2 2s^2 2p^5$ ; the bond forms using the one lone electron in F and the lone electron in H as a shared pair. This results in an overlap between the s orbital of the H and a p orbital of F. (There is an excellent animation of this at the following website of John Gelder from Oklahoma State University, who is a former Chief Reader for AP Chemistry: <http://intro.chem.okstate.edu/1515SP01/Lecture/Chapter10/Lec11601.html>.) The F atom retains three unshared pairs of electrons.

In both of the above cases, each of the bonding atoms contains an unpaired electron. However, some atoms contain fewer unpaired electrons than the number of bonds they form. In an effort to account for the behavior of such atoms (and the shapes of the molecules or ions formed), Pauling proposed that atomic orbitals on a single atom can be mixed or “hybridized” to form a set of composite hybrid orbitals. In this model, the new orbitals formed are all equal in energy, and the number of orbitals formed equals the number of orbitals mixed. A highly useful feature of the model is that the hybrid orbitals are mutually repulsive and their geometries can be used to describe the shapes of the resulting molecules.

1. Linus Pauling. *The Nature of the Chemical Bond*. 3rd ed. (Ithaca, NY: Cornell University, 1960).

A good example of hybridization occurs with  $\text{BeCl}_2$ . The electron configuration and the orbital diagrams of Be ( $1s^2 2s^2$ ) suggest that Be should not form bonds since all of its electrons are paired. However, if one of the two paired electrons in the Be s orbital is promoted to a p orbital and the s and the p orbitals are hybridized, each lone electron in one of the two sp hybrid orbitals can overlap with the lone electron in a p orbital on Cl to form  $\text{BeCl}_2$ .

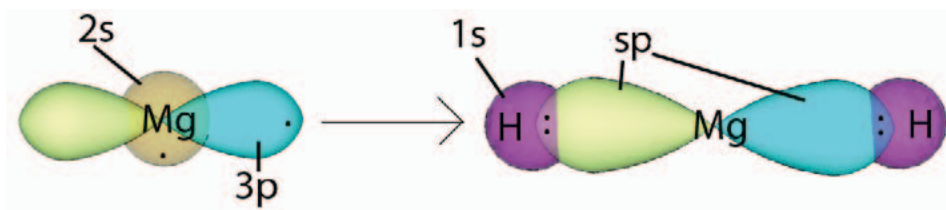
Methane,  $\text{CH}_4$ , provides another good example. The orbital diagram of C ( $1s^2 2s^2 2p^2$ ) shows two lone electrons, suggesting that it can only form two bonds. With promotion of one of the s electrons to a p orbital and the hybridization of the s and the three p orbitals to an  $sp^3$  state, C can form four bonds as it does in methane and other alkanes. Different combinations of the s and the three p orbitals can be envisioned to account for the existence of alkynes such as ethyne,  $\text{C}_2\text{H}_2$  (sp hybridization), and alkenes such as ethene,  $\text{C}_2\text{H}_4$  ( $sp^2$  hybridization).

The hybridization model also predicts shapes, based on the mutual bond repulsion of the hybrid orbitals. Thus, the four equivalent  $sp^3$  hybrid orbitals form a tetrahedral shape, as described below. For more advanced students who question how we know this happens, the answer is that hybridization is an “after the event” model, which attempts to account for the observed bonding and resulting molecular shapes rather than trying to predict them.

## Formation and Geometries of Hybrid Orbitals

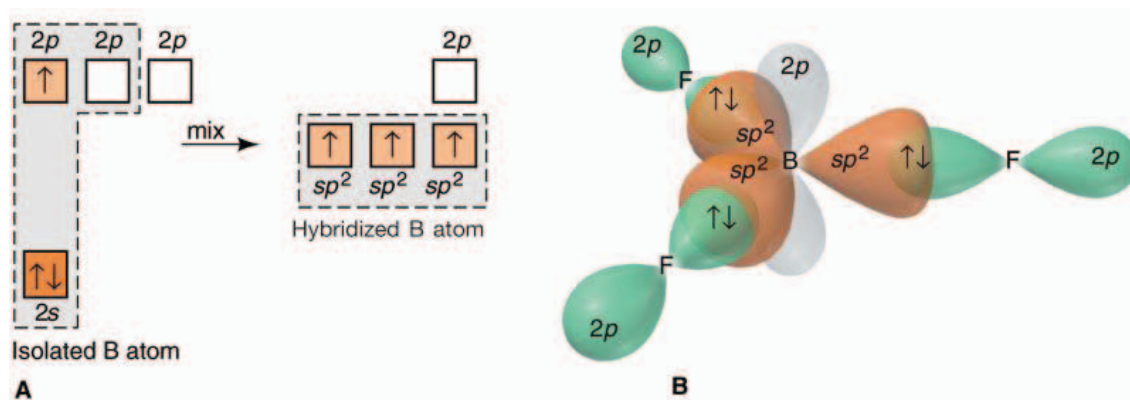
### sp Hybridization

The steps involved in the combination of an s and a p orbital to form two sp hybrid orbitals was described above. These sp orbitals are 180 degrees from each other to give a linear shape, as in magnesium hydride shown below.



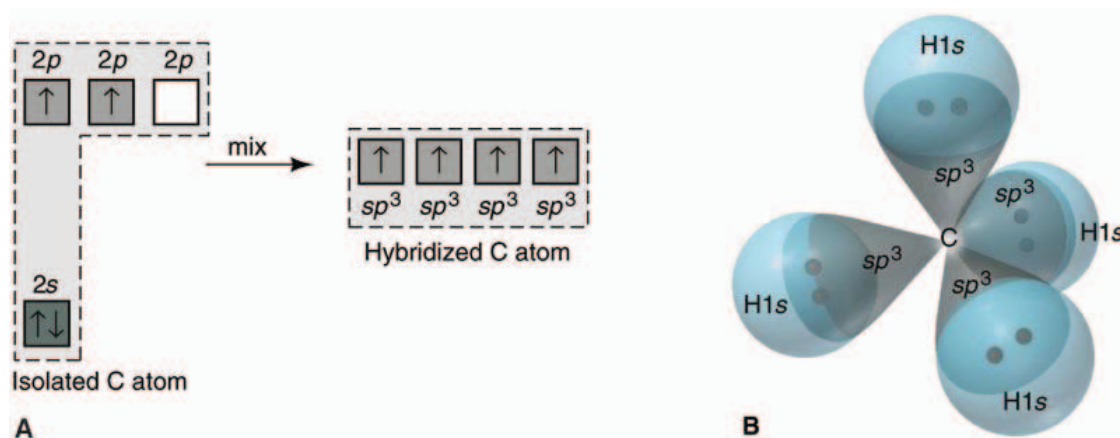
### $sp^2$ Hybridization

When one s orbital in an atom mixes with two p orbitals, the result is three  $sp^2$  orbitals. The superscript refers to the number of orbitals of a specified type that were mixed. This formation has one s and two p orbitals mixed. When these three hybrid orbitals overlap with an appropriate orbital from another atom, three sigma bonds are produced. An example is  $\text{BF}_3$ . This hybridization configuration gives a trigonal planar geometry with bond angles of 120 degrees.

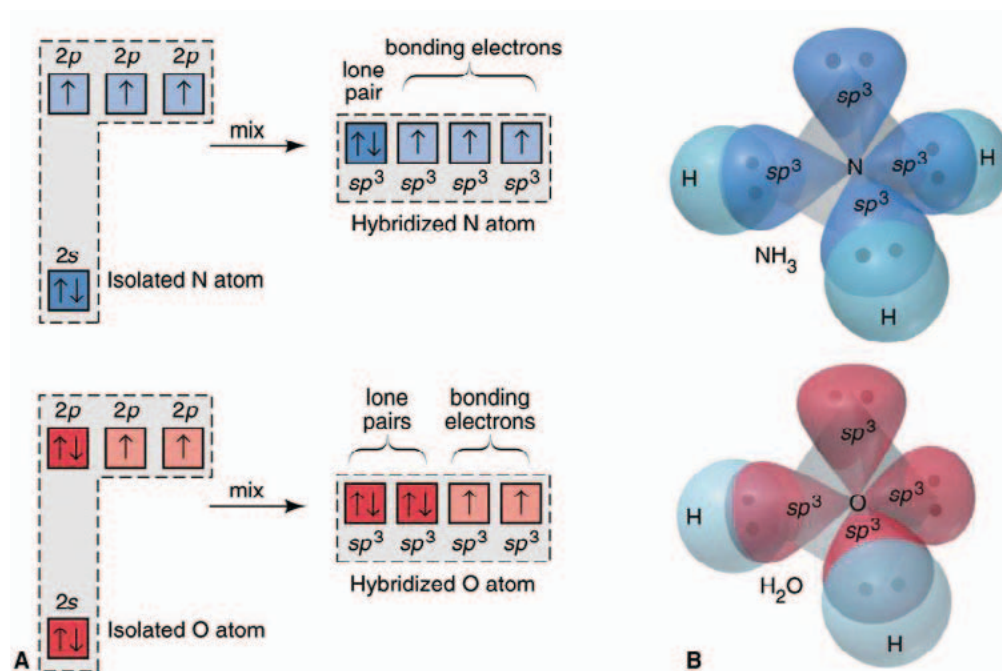


## $sp^3$ Hybridization

When one  $s$  orbital mixes with three  $p$  orbitals, the result is four  $sp^3$  orbitals. This hybridization and the mutual repulsion form four sigma bonds in the tetrahedral shape found in molecules such as  $CH_4$  and  $CF_4$ . However, if only three of the  $sp^3$  hybrids interact with other atoms to form sigma bonds, a pair of electrons remains in one  $sp^3$  hybrid. This is called a nonbonded or “lone pair.” The arrangement of the hybrid orbitals is still roughly tetrahedral, but the molecular shape is now trigonal pyramidal. An example of this behavior is found in  $NH_3$ . If two of the hybrid orbitals contain lone pairs, the resulting molecular shape is bent, as in  $H_2O$ . The angles in such molecules are not quite tetrahedral angles, and the extension of the model (VSEPR) suggests the lone pairs are allotted slightly more space than the sigma bonds. The following diagram shows the hybridization of  $CH_4$ .

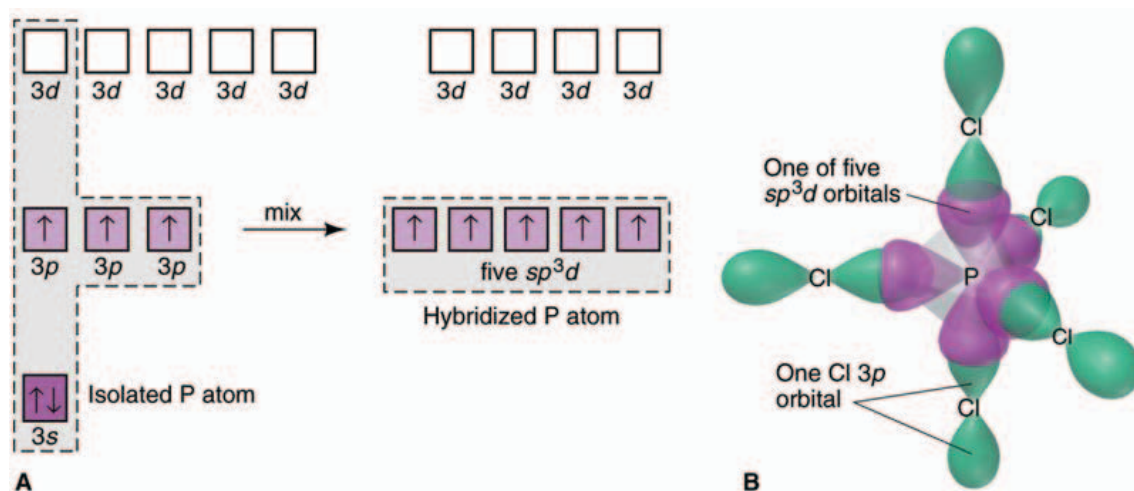


In contrast, the following diagram shows the  $sp^3$  of  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ .



## $sp^3d$ Hybridization

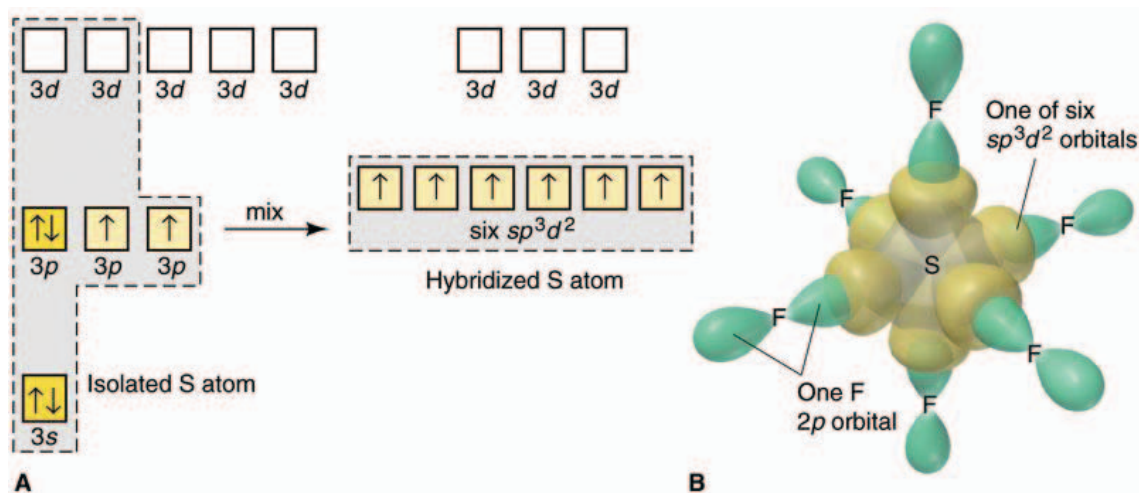
When an  $s$  orbital mixes with three  $p$  orbitals and one  $d$  orbital, the result is five  $sp^3d$  hybrid orbitals. When bonded to five other atoms via sigma bonds, an atom with this hybridization forms the trigonal bipyramidal arrangement found in such molecules as  $\text{PCl}_5$ . If one of the orbitals contains one, two or three lone pairs instead of bond pairs, the electron arrangement is still trigonal bipyramidal, but the molecular shapes are now seesaw (distorted tetrahedron), T-shaped and linear, respectively. Examples include  $\text{SF}_4$  (seesaw),  $\text{ClF}_3$  (T-shaped) and  $\text{XeF}_2$  (linear). This electron pair geometry is shown below for  $\text{PCl}_5$ .





## $sp^3d^2$ Hybridization

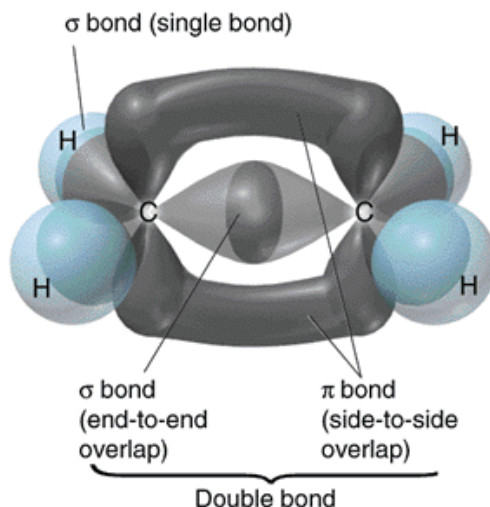
When an s orbital mixes with three p orbitals and two d orbitals, the result is six  $sp^3d^2$  orbitals. This hybridization results in the octahedral arrangement found in molecules such as  $SF_6$ , which is shown below. When bonding pairs are replaced by one or two lone pairs, the electron pair arrangement is still octahedral, but the shape is now square pyramidal or square planar, respectively. Examples include  $ClF_5$  (square pyramidal) and  $XeF_4$  (square planar).



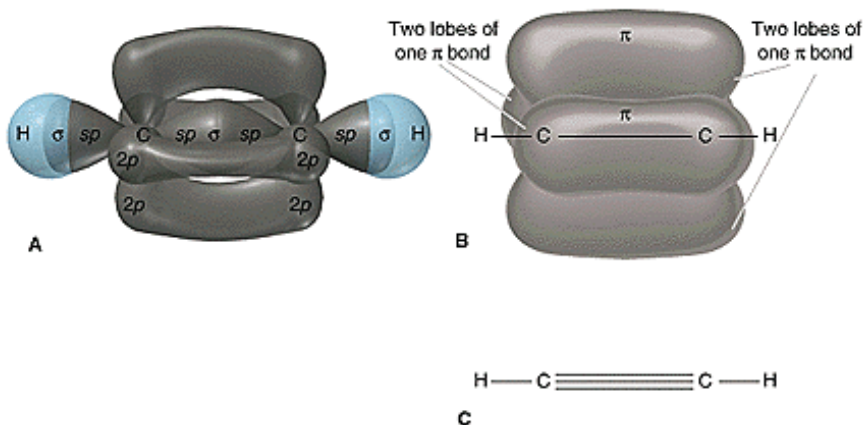
## Pi Bonds

The smaller atoms in the first main row of the periodic table may engage in a different type of bonding. If two atoms have at least one electron each in a p orbital, a side-to-side overlap can occur between the two p orbitals to form a pi molecular orbital or pi bond. This can happen up to two times between two adjacent atoms. The most common examples are ethene, in which the carbon is  $sp^2$  hybridized and forms one sigma and one pi bond between the carbon atoms; and ethyne ( $sp$  hybridized carbon), in which the two carbon atoms are joined by one sigma bond and two pi bonds. These two molecules are shown below.

### Ethene



## Ethyne



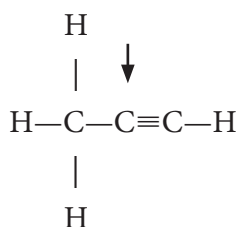
Other examples include N<sub>2</sub> with one sigma and two pi bonds and O<sub>2</sub> with one sigma and one pi bond.

## Sample Questions on Hybrid Orbitals and Sigma and Pi Bonding from AP Chemistry Examinations

On the AP Chemistry Exam, students have been asked about the hybridization of orbitals and its effect on the shape of molecules. They have not been asked directly about the shapes of the hybrid orbitals. This material is often linked to questions asking the students to draw Lewis dot structures. Several examples are given below.

### 2003

8(d) Given the structural formula for propyne below,



- (i) Indicate the hybridization of the carbon atom indicated by the arrow in the structure above.

*Answer:* In (i), the student needs to know that two areas are being used around the C, so the hybridization is *sp*.

- (ii) Indicate the total number of sigma ( $\sigma$ ) bonds and the total number of pi ( $\pi$ ) bonds in the molecule.

*Answer:* In (ii), the student needs to know that a triple bond is composed of one sigma bond and two pi bonds to correctly identify six sigma and two pi bonds in the molecule.

## 2004

7. Use appropriate chemical principles to account for each of the following observations. In each part, your response must include specific information about both substances.
- (c) The shape of the  $\text{ICl}_4^-$  ion is square planar, whereas the shape of the  $\text{BF}_4^-$  ion is tetrahedral.

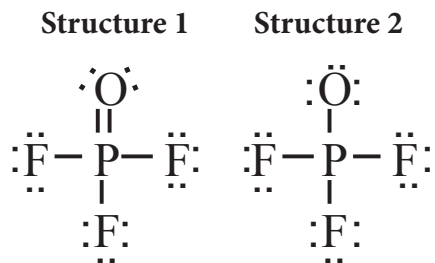
*Answer:*  $\text{ICl}_4^-$  uses  $\text{sp}^3\text{d}^2$  hybridization, four sigma bonds and two unshared electron pairs, while  $\text{BF}_4^-$  uses an  $\text{sp}^3$  hybridization and has no unshared electron pairs.

## 2005

- 6(b)(ii) What is the hybridization of the valence orbitals of P in  $\text{PF}_5$ ?

*Answer:*  $\text{sp}^3\text{d}$ .

- (c) Two Lewis structures can be drawn for the  $\text{OPF}_3$  molecule, as shown below.



- (i) How many sigma bonds and how many pi bonds are in Structure 1?

*Answer:* The student needs to understand that a double bond contains a sigma bond and a pi bond for a total of four sigma bonds and one pi bond. Many students have the misconception that a double bond is a pi bond.

## 2006

- 7(a)(ii) Identify the hybridization exhibited by the sulfur in the  $\text{SF}_3^+$  cation.

*Answer:* The answer is based on the structure the student had drawn in (a)(i).  $\text{sp}^3$ .

- 7(b)(ii) Identify the type of hybridization exhibited by the sulfur atom in the  $\text{SF}_5^-$  anion.

*Answer:* The answer is based on the structure drawn, but it should be  $\text{sp}^3\text{d}^2$ .

## 2006 Form B

6(b)(iii) What is the hybridization of the I atom in  $\text{ICl}_4^-$ ?

*Answer:*  $\text{sp}^3\text{d}^2$

## Teaching Tip

To teach this section, the best method is to have the students make and draw models, give the hybridization of the central atom, and count sigma and pi bonds in the total molecule. The students should have mastered the fundamentals of Lewis structures and electron “counting” before attempting hybridization. On the AP Exam, many students falter on questions because they have not first counted electrons correctly. Many beginning students find it confusing to distinguish between the hybrid *atomic* orbitals and the *molecular* orbitals that are the bonds in molecules, and they need considerable help and practice with many different examples. I also suggest using the following two websites to help students:

<http://intro.chem.okstate.edu/1515SP01/Lecture/Chapter10/Lec11601.html>

<http://www.science.uwaterloo.ca/~cchieh/cact/c120/hybrid.html>

# V. Bond and Molecular Polarity

David Hostage

## Bond Polarity: Electronegativity

Electronegativity (EN) is a concept that was developed by Linus Pauling from bond energy data for his classic book, *The Nature of the Chemical Bond*. He defined EN as “the power of an atom in a molecule to attract electrons to itself.” Subsequently, Robert Mulliken derived an EN scale as the average of the ionization energy and electron affinity of an atom.<sup>2</sup> Since that time, several other investigators have also developed EN scales based on other parameters,<sup>3</sup> but Pauling’s scale is still the most commonly used. Abbreviated as  $\chi$  (“chi”), the EN indicates the tendency of an atom in a molecule to attract electrons. Atoms with the smallest atomic radii and the largest effective nuclear charges have the largest electronegativities. Atoms with larger atomic radii have smaller electronegativities. Very electronegative atoms attract valence electrons, even to the point of acquiring additional electrons to become anions. As anions, their electronegativity becomes zero, since there they have no tendency to attract additional electrons. Similarly, a magnesium atom has a low electronegativity because it has little attraction for valence electrons, but a magnesium cation shows strong attraction for them.

Qualitatively, electronegativities increase from left to right across the periodic table and decrease down the table. To quantify these trends, Pauling originally assigned a value of 4.00 to fluorine, the most electronegative atom, and gave values to the atoms from fluorine to lithium that decreased by 0.5 units per element. At the lower left corner of the periodic table, the least electronegative element, cesium, has a value of 0.7. The EN of a particular atom varies slightly with its oxidation state and with the bonds that it forms, so the values in a table of electronegativities are average values. (Electronegativities have no units, since these values are comparative only.)

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2. R. S. Mulliken, “A New Electroaffinity Scale,” *Journal of Chemical Physics* 2 (1934): 782. For a more recent discussion, see also S. G. Bratsch, “Revised Mulliken electronegativities: II. Applications and limitations.” *Journal of Chemical Education* 65 (1988): (3), 223.

3. (a) A. L. Allred and E. G. Rochow, “Electronegativities of carbon, silicon, germanium, tin and lead.” *Journal of Inorganic and Nuclear Chemistry* 5 (1958): 269; A. L. Allred, “Electronegativity values from thermochemical data.” *Journal of Inorganic and Nuclear Chemistry* 17 (1961): 215.

(b) R. T. Sanderson, *Simple Inorganic Substances* (Malabar, FL: Krieger, Publishing), 23.

(c) L. C. Allen, “Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state free atoms.” *Journal of the American Chemical Society* 111 (1989): 9003; “Electronegativity scales.” *Accounts of Chemical Research* 23 (1990): 175; “Extension and completion of the periodic table” *Journal of the American Chemical Society* 114 (1992): 1510.

A bond between two atoms is called a covalent bond if it is between two nonmetals and an ionic bond if it involves a metal and a nonmetal. This implies that a stark difference exists between the two types of bonds; and while this is true for the extreme cases, there is actually a gradual transition. Originally, Pauling suggested that bonds with  $\Delta\chi > 0.5$  were ionic, but today the view is that there is a continuum of sharing possibilities, which range from equal sharing of valence electrons (nonpolar covalent bonds), to unequal sharing of those electrons (polar covalent bonds), to situations in which valence electrons are considered to have been transferred from one atom to another, resulting in ionic bonds. Many covalent bonds are polar, but the extent of the polarity varies. The absolute value of the difference between the two,  $\Delta\chi$ , gives a measure of the polarity of the bond. If the difference in EN ( $\Delta\chi$ ) is zero, as in a homonuclear diatomic molecule, the bond is referred to as a nonpolar covalent bond. A very large EN difference implies that the electrons in the bond spend most of the time with only one nucleus, thus producing an ionic bond. When the  $\Delta\chi$  is intermediate and the valence electrons are shared unequally, the bond is considered to be a polar covalent bond. Note that there is no abrupt change in  $\Delta\chi$ , thus there is no sharp difference between covalent and ionic bonds.

### Summary Table of Bond Types

Electronegativity difference, $\Delta\chi$	Bond type
None	Covalent
Medium	Polar covalent
Large	Ionic

## Periodic Table with Electronegativities

1A	2A	3B	4B	5B	6B	7B	8B					1B	2B	3A	4A	5A	6A	7A	8A
1 H 2.1																		2 He	
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne		
11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar		
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.9	28 Ni 1.9	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr 3.0		
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe 2.6		
55 Cs 0.7	56 Ba 0.9	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.9	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn 2.4		
87 Fr 0.7	88 Ra 0.9	89 Ac 1.1	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub								

58 Ce 1.1	59 Pr 1.1	60 Nd 1.1	61 Pm 1.2	62 Sm 1.2	63 Eu 1.1	64 Gd 1.2	65 Tb 1.2	66 Dy 1.2	67 Ho 1.2	68 Er 1.2	69 Tm 1.2	70 Yb 1.2	71 Lu 1.3
90 Th 1.3	91 Pa 1.5	92 U 1.7	93 Np 1.3	94 Pu 1.3	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.5	103 Lr

### Exercise

Indicate the type of bond expected to form between the two indicated atoms. If it is polar covalent, place a “ $\delta^-$ ” to indicate the negative end of any dipole formed.

- H - H
- H - O
- H - N
- H - C
- H - F
- Na - Cl
- Cl - F

Answers:

(a) nonpolar covalent; (b) polar covalent,  $\delta^-$  at O; (c) polar covalent,  $\delta^-$  at N;  
(d) essentially nonpolar covalent; (e) polar covalent,  $\delta^-$  at F; (f) ionic; (g) polar covalent,  
 $\delta^-$  at F

## Molecular Geometry and Molecular Polarity

Polarity is a measurable characteristic of compounds that influences physical properties, such as melting and boiling points, solubility, and intermolecular forces between molecules. For the most part, there is a direct relation between the polarity of a molecule and the number and type of covalent bonds, polar or nonpolar, that are present. In some instances, a molecule may have polar bonds, but those bonds may be oriented in such a manner that a nonpolar molecule results.

Polarity results from the uneven electron distribution between and among nuclei. This can lead to partial charge distribution between the atoms in a compound. Electrons in a polar covalent bond are not shared equally between the two atoms forming the bond. This causes partial positive and negative charges, with the negative end ( $\delta^-$ ) toward the nucleus and having greater attraction for the valence electrons and with the other end ( $\delta^+$ ) at the less electronegative nucleus. The physical separation of the partial charges creates a dipole. The word *dipole* implies two poles, or separated partial positive and negative charges. More electronegative atoms, such as fluorine, oxygen, nitrogen and the halogens, tend to have partial negative charges when paired with less electronegative bond partners like hydrogen and carbon, which then have partial positive charges.

Nonpolar molecules are of two types: (1) those which are nonpolar due to the atoms having the same (or very nearly the same) EN values, and (2) those which are nonpolar, despite having polar bonds, because those bonds are oriented so that the dipoles cancel one another. Homonuclear diatomic molecules (formed when two identical nuclei bond) are nonpolar by definition, since there can be no difference in electronegativities between identical nuclei. Examples of such substances include the homonuclear diatomic species  $H_2$ ,  $N_2$  and  $O_2$ , and the halogens  $F_2$ ,  $Cl_2$ ,  $Br_2$  and  $I_2$ . In addition, there are other molecules whose atoms may have such a small electronegativity difference that their dipole moments are zero or very small. Examples of these include the hydrocarbons such as  $CH_4$ ,  $C_2H_6$ , etc.

### Effect of molecular geometry on molecular polarity

The second type of nonpolar molecule contains two or more polar bonds or lone pairs of electrons but has a molecular geometry that leads to the bond dipoles or the lone pairs canceling one other. This idea is similar to vector analysis in physics, where vectors of equal length but opposing directions lead to a net force of zero. Just as polar bonds can be placed in a symmetrical arrangement such that individual bond polarities cancel each other to give a molecule that is not polar, lone pairs of electrons (nonbonding pairs) can be placed in



such a way that symmetry cancels any polarity. Examples of nonpolar species that contain polar bonds include carbon dioxide ( $\text{CO}_2$ , linear), boron trifluoride ( $\text{BF}_3$ , trigonal planar), carbon tetrafluoride or tetrafluoromethane ( $\text{CF}_4$ , tetrahedral), phosphorus pentafluoride ( $\text{PF}_5$ , trigonal bipyramidal) and sulfur hexafluoride ( $\text{SF}_6$ , octahedral). Examples of molecules that are nonpolar despite containing both polar bonds and lone pairs of electrons on the central atom include xenon difluoride ( $\text{XeF}_2$ , linear molecule based on trigonal bipyramidal electron pair geometry) and xenon tetrafluoride ( $\text{XeF}_4$ , square planar molecular geometry with octahedral electron pair geometry). Draw these structures and notice how the individual bond polarities and lone electron pairs cancel.

## Exercise

Draw a Lewis structure for each species and indicate if it is polar by placing “ $\delta^-$ ” at the negative end of any dipole formed.

- (a) carbon tetrachloride,  $\text{CCl}_4$
- (b) iodine trichloride,  $\text{ICl}_3$
- (c) hydrocyanic acid,  $\text{HCN}$
- (d) iodine pentafluoride,  $\text{IF}_5$

*Answers:*

- (a) tetrahedral, nonpolar; (b) T-shaped,  $\delta^-$  at equatorial Cl; (c) linear,  $\delta^-$  at N;
- (d) square pyramidal,  $\delta^-$  at apical F

Resonance structures, where more than one satisfactory Lewis structure can be drawn for a given species, can also describe the position of electrons in space. The actual structure of the molecules is intermediate between (or among) the different resonance structures. An example of this is the molecule sulfur trioxide,  $\text{SO}_3$ , which has two single bonds and one double bond to sulfur in each Lewis structure. Rather than exhibiting a double and two single bonds, the three S-O bonds are equivalent with one pair of electrons delocalized across the molecule. Because of this distribution of electrons,  $\text{SO}_3$  is a nonpolar molecule. Draw the three Lewis structures.

## Exercise

Draw a Lewis structure for each species, including all resonance structures. If the species is polar, indicate by placing “ $\delta^-$ ” at the negative end of the dipole.

- (a) sulfur dioxide,  $\text{SO}_2$
- (b) dinitrogen monoxide,  $\text{N}_2\text{O}$
- (c) nitrogen dioxide,  $\text{NO}_2$
- (d) carbon oxysulfide,  $\text{SCO}$

*Answers:*

- (a) two resonance forms,  $\delta^-$  midway between Os; (b) two resonance forms,  $\delta^-$  at O; (c) two resonance forms,  $\delta^-$  midway between Os; (d) three resonance forms,  $\delta^-$  at O

## Effect of lone pairs of electrons

A polar molecule results when a molecule contains polar bonds in an unsymmetrical arrangement. Often these molecules also include lone pairs (nonbonding pairs) of electrons. Lone pairs of electrons often lead to unequal charge distributions, with the lone pairs constituting the negative end of the dipole, although the assignment depends on the atoms involved. For example, in ammonia,  $\text{NH}_3$  (trigonal pyramidal molecule with a lone pair of electrons on the N giving a tetrahedral electron pair geometry), the  $\delta^-$  is associated with the lone pair on the N atom. On the other hand, in nitrogen trifluoride,  $\text{NF}_3$  (which is also pyramidal but has a very small dipole moment), the  $\delta^-$  is at the fluorine end of the molecule due to the high EN of the F atoms. Other examples of polar molecules that contain one or more lone pairs of electrons include hydrogen sulfide ( $\text{H}_2\text{S}$ , bent molecule based on tetrahedron), sulfur tetrafluoride ( $\text{SF}_4$ , seesaw variation of trigonal bipyramidal), chlorine trifluoride ( $\text{ClF}_3$ , T-shaped variation on trigonal bipyramidal) and  $\text{BrF}_5$  (square pyramidal variation of octahedral). A complete understanding of the valence shell electron pair repulsion theory is important to allow prediction of molecular polarity. The following table summarizes the effect of lone pairs on molecular polarity:

Summary of Electron Geometries, Molecular Geometries and Molecular Polarities

Electron regions	Electron region geometry	Bonding regions	Nonbonding regions	Molecular geometry	Polarity	Example
2	Linear	2	0	Linear	No	$\text{CO}_2$
3	Trigonal planar	3	0	Trigonal planar	No	$\text{BH}_3$
		2	1	Bent	Yes	$\text{SO}_2$
4	Tetrahedral	4	0	Tetrahedral	No	$\text{CH}_4$
		3	1	Trigonal pyramidal	Yes	$\text{NH}_3$
		2	2	Bent	Yes	$\text{H}_2\text{O}$
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	No	$\text{PCl}_5$
		4	1	Seesaw	Yes	$\text{SCl}_4$
		3	2	T-shaped	Yes	$\text{ICl}_3$
		2	3	Linear	No	$\text{XeCl}_2$
6	Octahedral	6	0	Octahedral	No	$\text{SCl}_6$
		5	1	Square pyramidal	Yes	$\text{ICl}_5$
		4	2	Square planar	No	$\text{XeCl}_4$

## Exercise

Draw a Lewis structure for each species. Use the VSEPR theory to determine the electron pair geometry, then use that answer to determine the molecular geometry. Predict whether each species is polar or nonpolar.

- (a)  $\text{CCl}_4$
- (b)  $\text{H}_2\text{Se}$
- (c)  $\text{ClF}_3$
- (d)  $\text{XeO}_3$
- (e)  $\text{RnF}_2$
- (f)  $\text{BeH}_2$

Answers:

(a) tetrahedral, nonpolar; (b) bent linear, polar; (c) T-shaped, polar; (d) trigonal pyramidal, polar; (e) linear, nonpolar; (f) linear, nonpolar

## Sources for Graphics

(Images #33, 34, 37–43) Silberberg, Martin. *Chemistry: The Molecular Nature of Matter and Change*, 4th edition. New York, NY; The McGraw-Hill Companies, Inc., 2006.

Image 35: [http://chemwiki.ucdavis.edu/Organic\\_Chemistry/Fundamentals/Hybrid\\_Orbitals](http://chemwiki.ucdavis.edu/Organic_Chemistry/Fundamentals/Hybrid_Orbitals)

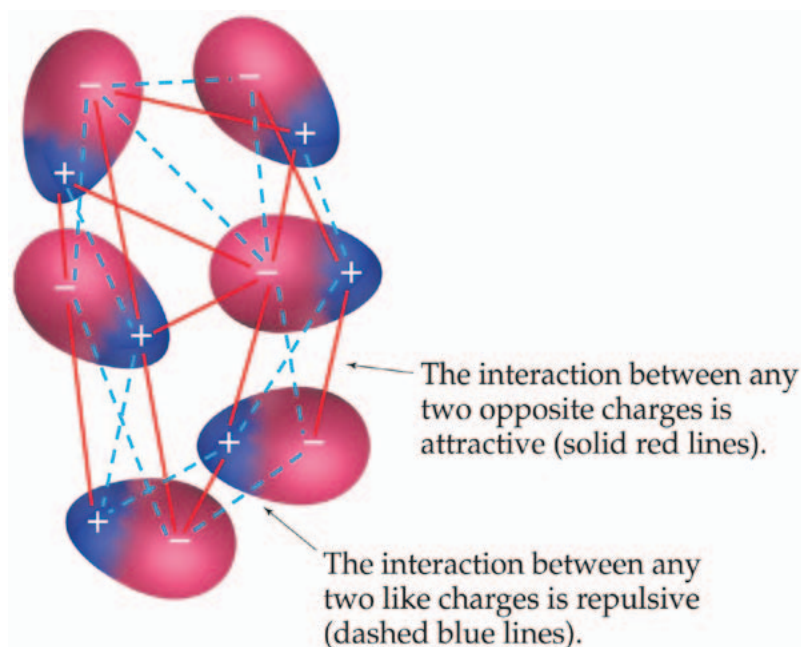
# VI. Intermolecular Attractions

Valerie Ferguson

The attractions between molecules are much weaker than the covalent bonds within the molecules. These attractions vary depending on the nature of the molecules.

## Dipole-Dipole

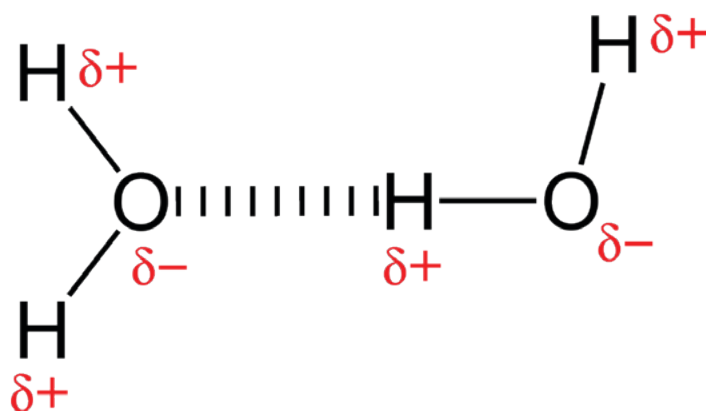
Many molecules have permanent dipoles. These polar covalent molecules form attractions between the positive end of one molecule and the negative end of an adjacent molecule. These dipole-dipole attractions are greater than the like-charge repulsions. Dipole-dipole attractions are effective over very short distances between molecules. This attraction decreases sharply as the distance between adjacent molecules increases. This type of attraction is generally stronger for molecules with greater permanent dipole moments.



It is important for teachers to stress that dipole-dipole attractions are very weak compared to ionic or covalent bonds. For example, dipole-dipole attractions are about 1 percent as strong as a covalent bond.

## Hydrogen Bonding

Strong dipole-dipole attractions occur in molecules containing hydrogen covalently bonded to a nitrogen, oxygen or fluorine atom. The attraction occurs between the hydrogen covalently bonded to a nitrogen, oxygen or fluorine in one molecule and the nitrogen, oxygen or fluorine on an adjacent molecule. The covalent bonds within the molecules are quite polar due to the small sizes of the atoms involved. The hydrogen in these covalent bonds has a partial positive charge, since there are no inner core electrons and the shared electrons are strongly attracted to the small, very electronegative atoms. The attractions that develop between these molecules are about four to five times stronger than other dipole-dipole attractions and are called *hydrogen bonding*. Hydrogen bonding is responsible for the unusual properties of water and is very important in biological systems such as proteins and DNA/RNA.



### Teaching Tip

Due to the similarity in terms, it is important to emphasize that hydrogen bonding is still less than 10 percent of the strength of a covalent bond. Hydrogen bonding is thus a weak intermolecular attraction.

## London Dispersion Forces

Nonpolar molecules do not have permanent dipoles. At any given instant, the electrons may be unevenly distributed within an atom or molecule. The electrons of nearby atoms or molecules will be repelled by the temporary concentration of electrons in the first molecule. The second atom or molecule will have a momentary positive end that will be attracted to the electrons of the first molecule. This process is repeated many times. Atoms and molecules with more electrons are more likely to form these instantaneous dipoles and the subsequent induced dipoles. The electron clouds of such particles are easier to

distort since there is less attraction of the electrons to their own positively charged nuclei. These electron clouds are said to be more polarizable. The greater the polarizability, the greater the extent of the induced dipoles and the stronger the dispersion forces between particles. Although the number of electrons increases with an increase in the molar mass of molecules, it is important to understand that dispersion forces are not simply a consequence of changes in molar mass and should *not* be explained in those terms.

Because melting points (MPs) and boiling points (BPs) of covalent molecules increase with the strengths of the forces holding them together, it is common to use MPs and BPs as a way to compare the strengths of intermolecular forces. This is shown below, with the molecular formulas, molar masses and normal BPs of the first five straight-chain hydrocarbons.

<u>Molecular Formula</u>	<u>Molar Mass</u>	<u>Normal BP (C)</u>
CH <sub>4</sub>	16	-161.5
C <sub>2</sub> H <sub>6</sub>	30	-88.5
C <sub>3</sub> H <sub>8</sub>	44	-42.1
C <sub>4</sub> H <sub>10</sub>	58	-0.5
C <sub>5</sub> H <sub>12</sub>	72	36.1

In addition, intermolecular forces often depend on other factors, such as molecular shape, as the following data for the isomers of pentane, C<sub>5</sub>H<sub>12</sub>, show.

<u>Name</u>	<u>Structure</u>	<u>Normal BP (C)</u>
n-pentane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	36.1
2-methylbutane	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub>	27.9
2,2-dimethylpropane	(CH <sub>3</sub> ) <sub>4</sub> C	9.5

This difference in BPs is attributed to the way the molecules pack together. Thus n-pentane has long skinny molecules that pack together more tightly and exhibit stronger dispersion forces than either 2-methylbutane, with a branched structure, or 2,2-dimethylpropane, with a short globular one.

For molecules with similar molar masses, dispersion forces have a smaller effect on physical properties than dipole-dipole attractions or hydrogen bonds, as shown by the data below.

<u>Molecular Formula</u>	<u>Molar Mass</u>	<u>Normal BP (C)</u>	<u>Strongest IMF</u>
C <sub>3</sub> H <sub>8</sub>	44	-42.1	dispersion forces
CH <sub>3</sub> OCH <sub>3</sub>	46	-23	dipole-dipole
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	45	16.6	H-bonding
C <sub>2</sub> H <sub>5</sub> OH	46	78.5	H-bonding

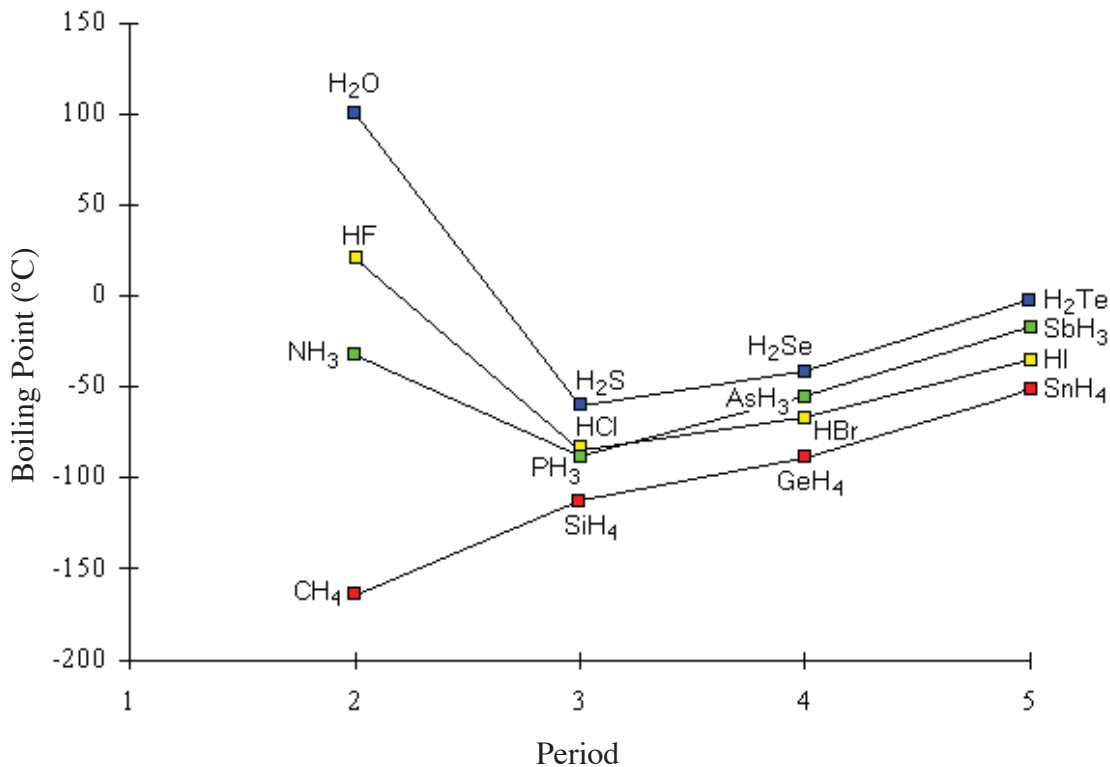
However, when comparing molecules with a disparity in molar mass, the molecule with the greater molar mass, and therefore more polarizable electrons, will have greater dispersion forces. The dispersion forces may have a greater effect on physical properties.

Thus, while  $\text{H}_2\text{O}$  has an unusually high normal BP (100 C) for a molecule with its molar mass ( $M = 18$ ), its BP is less than the BP (126 C) of n-octane,  $\text{C}_8\text{H}_{18}$ , ( $M = 114$ ), even though the latter substance exhibits only dispersion forces.

## Summary

Many physical properties are dependent upon intermolecular attractions. Variations in physical properties between substances can be attributed to variations in the intermolecular attractions. These relationships are covered regularly on the AP Exam. Students should be able to explain variations in physical properties by giving the reasons for the difference in strength of intermolecular attractions. Physical properties that are commonly used are melting point and boiling point.

The graph below is a typical presentation of boiling points of substances versus molar mass. The boiling points of the Group IVA substances increase with an increase in molar mass, as do those for the heavier members of the other three families of hydrides. The dominant intermolecular forces for all of these substances are dispersion forces. However, the three compounds that exhibit hydrogen-bonding ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$ ) show distinctly higher BPs than expected on the basis of their molar masses.



## Sample Questions from AP Chemistry Examinations

### 2004 Question 7

Use appropriate chemical principles to account for each of the following observations. In each part, your response *must* include specific information about *both* substances.

- (a) At 25°C and 1 atm, F<sub>2</sub> is a gas, whereas I<sub>2</sub> is a solid.

*Answer:* Both F<sub>2</sub> and I<sub>2</sub> are nonpolar, so the only intermolecular attractive forces are London dispersion forces. I<sub>2</sub> is solid because the electrons in the I<sub>2</sub> molecules occupy a larger volume and are more polarizable compared to the electrons in the F<sub>2</sub> molecules. As a result, the dispersion forces are considerably stronger in I<sub>2</sub> compared to F<sub>2</sub>.

Students often neglect to address both of the substances compared in a question; the directions now usually remind students to describe both substances. Students will fail to state that both molecules are nonpolar. Students then need to explain that the dispersion forces between I<sub>2</sub> molecules are greater due to the greater number of polarizable electrons.

- (d) Ammonia, NH<sub>3</sub>, is very soluble in water, whereas phosphine, PH<sub>3</sub>, is only moderately soluble.

Ammonia has hydrogen-bonding intermolecular forces, whereas phosphine has dipole-dipole and/or dispersion intermolecular forces. Water also has hydrogen-bonding intermolecular attractive forces. Ammonia is more soluble in water than phosphine because ammonia molecules can hydrogen-bond with water molecules, whereas phosphine molecules cannot hydrogen-bond with water molecules.

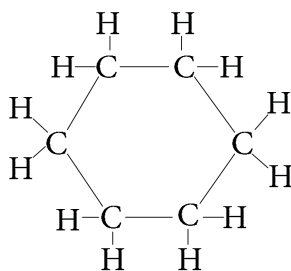
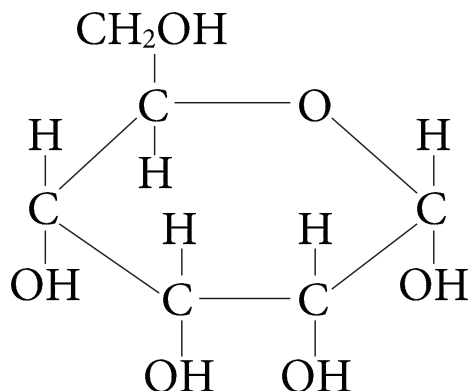
Students commonly neglect to state the most important forces in each substance. Students should then link together the type of attraction to the relative strength of each attractive force.



**2006 Question 6**

Answer each of the following in terms of principles of molecular behavior and chemical concepts.

- (a) The structures for glucose,  $C_6H_{12}O_6$ , and cyclohexane,  $C_6H_{12}$ , are shown below.



Identify the type(s) of intermolecular attractive forces in:

- (i) pure glucose

*Answer:* Hydrogen bonding OR dipole-dipole interactions OR van de Waals interactions. (London dispersion forces may also be mentioned.)

- (ii) pure cyclohexane

*Answer:* London dispersion forces

- (b) Glucose is soluble in water but cyclohexane is not soluble in water. Explain.

*Answer:*

- Glucose is polar and cyclohexane is nonpolar.
- Polar solutes (such as glucose) are generally soluble in polar solvents such as water.
- Nonpolar solutes (such as cyclohexane) are not soluble in the polar solvent.

Students generally answered Part a of this question correctly. Students seemed to have trouble differentiating between intermolecular and intramolecular forces throughout this question.

Similar topics and/or terms should not be introduced at the same time, if possible. If the text you are using includes intermolecular and intramolecular bonding in the same chapter, you may want to consider adjusting the sequence.

## 2005 Question 7

Use principles of atomic structure, bonding and/or intermolecular forces to respond to each of the following. Your response *must* include specific information about *all* substances referred to in each question.

- (a) At a pressure of 1 atm, the boiling point of  $\text{NH}_3(l)$  is 240 K, whereas the boiling point of  $\text{NF}_3(l)$  is 144 K.

(i) Identify the intermolecular force(s) in each substance.

*Answer:*  $\text{NH}_3$  has dispersion forces and hydrogen-bonding forces.  $\text{NF}_3$  has dispersion forces and dipole-dipole forces. (Credit earned for hydrogen-bonding and dipole-dipole forces.)

(ii) Account for the differences in the boiling points of the substances.

*Answer:* The higher boiling point for  $\text{NH}_3$  is due to the greater strength of the hydrogen-bonding intermolecular attractive forces among  $\text{NH}_3$  molecules compared to that of the dipole-dipole attractive forces among  $\text{NF}_3$  molecules.

## 2001 Question 8

Account for each of the following observations about pairs of substances. In your answers, use appropriate principles of chemical bonding and/or intermolecular forces. In each part, your answer must include references to *both* substances.

- (a) Even though  $\text{NH}_3$  and  $\text{CH}_4$  have similar molecular masses,  $\text{NH}_3$  has a much higher normal boiling point ( $-35^\circ\text{C}$ ) than  $\text{CH}_4$  ( $-164^\circ\text{C}$ ).

*Answer:*  $\text{NH}_3$  has hydrogen bonding between molecules (or dipole-dipole interactions between molecules) and  $\text{CH}_4$  has London dispersion forces. The intermolecular forces in  $\text{NH}_3$  are stronger than those in  $\text{CH}_4$ . (No credit is earned for a discussion of lone pairs of electrons. No credit is earned for saying only that  $\text{NH}_3$  is polar and  $\text{CH}_4$  is nonpolar, with no more discussion.)

This question states that  $\text{NH}_3$  and  $\text{CH}_4$  have similar molar masses. Students then need to focus their responses on the intermolecular attractions of each. Remind your students to state which forces are stronger for each situation. They need to demonstrate an understanding of the relative strengths of the intermolecular forces and the relevance to molecular properties.

## 2002 Multiple-Choice Questions

67. Which of the following describes the changes in forces of attraction that occur as  $\text{H}_2\text{O}$  changes phase from a liquid to a vapor?
- (a) H-O bonds break as H-H and O-O bonds form.
  - (b) Hydrogen bonds between  $\text{H}_2\text{O}$  molecules are broken.
  - (c) Covalent bonds between  $\text{H}_2\text{O}$  molecules are broken.
  - (d) Ionic bonds between  $\text{H}^+$  ions and  $\text{OH}^-$  ions are broken.
  - (e) Covalent bonds between  $\text{H}^+$  ions and  $\text{H}_2\text{O}$  molecules become more effective.

Answer: B.

70. Of the following pure substances, which has the highest melting point?
- (a)  $\text{S}_8$
  - (b)  $\text{I}_2$
  - (c)  $\text{SiO}_2$
  - (d)  $\text{SO}_2$
  - (e)  $\text{C}_6\text{H}_6$

Answer: C.

## Suggested Websites

The visual representations in the websites below are very helpful for students. The attractions between such small particles are often difficult for students to conceptualize.

<http://library.tedankara.k12.tr/webchem/Chemical%20bonding%20and%20intermolecular%20forces/Intermolecular%20Forces.htm>

<http://intro.chem.okstate.edu/1515SP01/Lecture/Chapter12/Lec2201.html>

<http://antoine.frostburg.edu/chem/senese/101/liquids/faq/h-bonding-vs-london-forces.shtml>

## Laboratory and Demonstrations

### Evaporation and Intermolecular Attractions

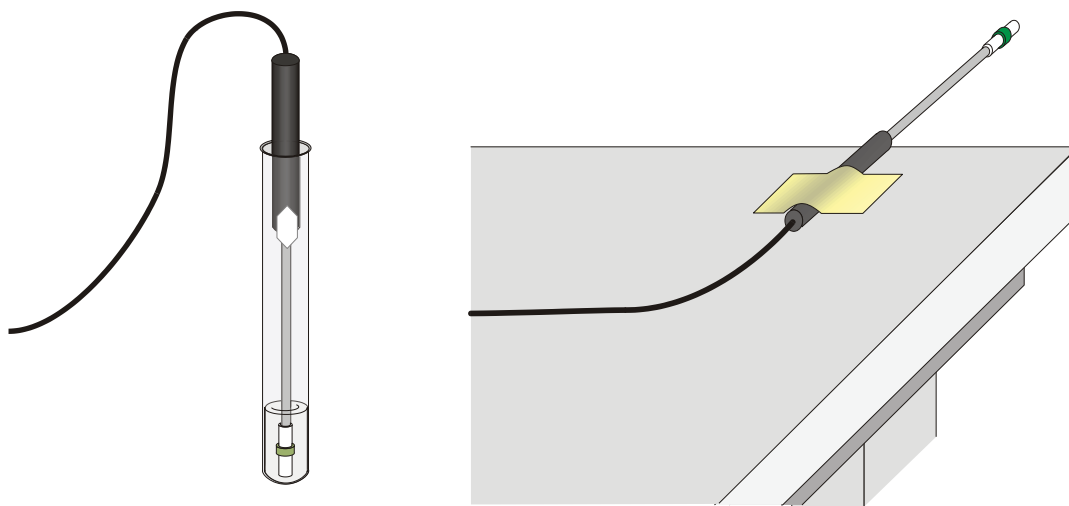
[From Dan D. Holmquist, Jack Randall, and Donald L. Volz. "Evaporation and Intermolecular Attractions," *Chemistry with Calculators* (Beaverton, OR: Vernier Software and Technology).]

This activity compares the change in temperature during evaporation of three different liquids. The magnitude of the temperature decrease is related to the strength of the intermolecular attractions. The liquids recommended include *n*-pentane, *n*-hexane, methanol, ethanol, 1-propanol and 1-butanol.

## Student Directions

In this experiment, temperature probes are placed in various liquids. Evaporation occurs when the probe is removed from the liquid's container. This evaporation is an endothermic process that results in a temperature decrease. The magnitude of a temperature decrease is, like viscosity and boiling temperature, related to the strength of intermolecular forces of attraction. In this experiment, you will study temperature changes caused by the evaporation of several liquids and relate the temperature changes to the strength of intermolecular forces of attraction. You will use the results to predict, and then measure, the temperature change for several other liquids.

You will encounter two types of organic compounds in this experiment — alkanes and alcohols. The two alkanes are pentane,  $C_5H_{12}$ , and hexane,  $C_6H_{14}$ . In addition to carbon and hydrogen atoms, alcohols also contain the -OH functional group. Methanol,  $CH_3OH$ , and ethanol,  $C_2H_5OH$ , are two of the alcohols that we will use in this experiment. You will examine the molecular structure of alkanes and alcohols for the presence and relative strength of two intermolecular forces — hydrogen bonding and dispersion forces.



## Materials

LabPro or CBL 2 interface	methanol (methyl alcohol)
Ti graphing calculator	ethanol (ethyl alcohol)
DataMate program	1-propanol
2 temperature probes	1-butanol
6 pieces of filter paper (2.5 cm X 2.5 cm)	<i>n</i> -pentane
2 small rubber bands	<i>n</i> -hexane
masking tape	

## Pre-Lab Exercise

Prior to doing the experiment, complete the pre-lab table. The name and formula are given for each compound. Draw a structural formula for a molecule of each compound. Then determine the molecular weight of each of the molecules. Dispersion forces exist between any two molecules, and they generally increase as the molecular weight of the molecule increases. Next, examine each molecule for the presence of hydrogen bonding. Before hydrogen bonding can occur, a hydrogen atom must be bonded directly to an N, O or F atom within the molecule. Tell whether or not each molecule has hydrogen-bonding capability.

## Procedure

- Obtain and wear goggles! **Caution:** *The compounds used in this experiment are flammable and poisonous. Avoid inhaling their vapors and having your skin or clothing come into contact with the compounds. Be sure there are no open flames in the lab during this experiment. Notify your teacher immediately if an accident occurs.*
- Plug Temperature Probe 1 into Channel 1 and Temperature Probe 2 into Channel 2 of the LabPro or CBL 2 interface. Use the link cable to connect the TI graphing calculator to the interface. Firmly press in the cable ends.
- Turn on the calculator and start the DATAMATE program. Press  to reset the program.
- Set up the calculator and interface for two temperature probes.
  - Select SETUP from the main screen.
  - If the calculator displays two temperature probes, one in CH 1 and another in CH 2, proceed directly to step 5. If it does not, continue with this step to set up your sensor manually.
  - Press  to select CH 1.
  - Select TEMPERATURE from the SELECT SENSOR menu.
  - Select the temperature probe you are using (in °C) from the TEMPERATURE menu.
  - Press  once; and then press  to select CH2.
  - Select TEMPERATURE from the SELECT SENSOR menu.
  - Select the temperature probe you are using (in °C) from the TEMPERATURE menu.
- Set up the data-collection mode.
  - To select MODE, use  to move the cursor to MODE, and press .

- b. Select TIME GRAPH from the SELECT MODE menu.
  - c. Select CHANGE TIME SETTINGS from the TIME GRAPH SETTINGS menu.
  - d. Enter “3” as the time between samples in seconds.
  - e. Enter “80” as the number of samples. (The length of the data collection will be four minutes.)
  - f. Select OK to return to the setup screen.
  - g. Select OK again to return to the main screen.
6. Wrap Probe 1 and Probe 2 with square pieces of filter paper secured by small rubber bands as shown in the figures above. Roll the filter paper around the probe tip in the shape of a cylinder. Hint: First slip the rubber band up on the probe, wrap the paper around the probe, and then finally slip the rubber band over the wrapped paper. The paper should be even with the probe end.
  7. Stand Probe 1 in the ethanol container and Probe 2 in the 1-propanol container. Make sure the containers do not tip over.
  8. Prepare two pieces of masking tape, each about 10-cm long, to be used to tape the probes in position during step 9.
  9. After the probes have been in the liquids for at least 30 seconds, select START to begin collecting temperature data. A live graph of temperature versus time for both Probe 1 and Probe 2 is being plotted on the calculator screen. The live readings are displayed in the upper-right corner of the graph, Probe 1 first, Probe 2 below. Monitor the temperature for 15 seconds to establish the initial temperature of each liquid. Then simultaneously remove the probes from the liquids and tape them so the probe tips extend 5 cm over the edge of the table top as shown in the figures above.
  10. Data collection will stop after four minutes (or press the  key to stop *before* four minutes have elapsed). On the displayed graph of temperature versus time, each point for Probe 1 is plotted with a dot, and each point for Probe 2 with a box. As you move the cursor right or left, the time (X) and temperature (Y) values of each Probe 1 data point are displayed below the graph. Based on your data, determine the maximum temperature,  $t_1$ , and minimum temperature,  $t_2$ . Record  $t_1$  and  $t_2$  for Probe 1.  
  
Press  to switch the cursor to the curve of temperature versus time for Probe 2. Examine the data points along the curve. Record  $t_1$  and  $t_2$  for Probe 2.
  11. For each liquid, subtract the minimum temperature from the maximum temperature to determine  $\Delta t$ , the temperature change during evaporation.
  12. Roll the rubber band up the probe shaft and dispose of the filter paper as directed by your instructor.

- Based on the  $\Delta t$  values you obtained for these two substances, plus information in the pre-lab exercise, *predict* the size of the  $\Delta t$  value for 1-butanol. Compare its hydrogen-bonding capability and molecular weight to those of ethanol and 1-propanol. Record your predicted  $\Delta t$ , then explain how you arrived at this answer in the space provided. Do the same for *n*-pentane. It is not important that you predict the exact  $\Delta t$  value; simply estimate a logical value that is higher, lower, or between the previous  $\Delta t$  values.
- Press  to return to the main screen. Test your prediction in step 13 by repeating steps 6–12 using 1-butanol with Probe 1 and *n*-pentane with Probe 2.
- Based on the  $\Delta t$  values you have obtained for all four substances, plus information in the pre-lab exercise, predict the  $\Delta t$  values for methanol and *n*-hexane. Compare the hydrogen-bonding capability and molecular weight of methanol and *n*-hexane to those of the previous four liquids. Record your predicted  $\Delta t$ , and then explain how you arrived at this answer in the space provided.
- Press  to return to the main screen. Test your prediction in step 15 by repeating steps 6–12, using methanol with Probe 1 and *n*-hexane with Probe 2.

## Processing the Data

- Two of the liquids, *n*-pentane and 1-butanol, had nearly the same molecular weights, but significantly different  $\Delta t$  values. Explain the difference in  $\Delta t$  values of these substances, based on their intermolecular forces.
- Which of the alcohols studied has the strongest intermolecular forces of attraction? Which has the weakest intermolecular forces? Explain using the results of this experiment.
- Which of the alkanes studied has the stronger intermolecular forces of attraction? Which has the weaker intermolecular forces? Explain using the results of this experiment.
- Plot a graph of  $\Delta t$  values of the four alcohols versus their respective molecular weights. Plot molecular weight on the horizontal axis and  $\Delta t$  on the vertical axis.

**Pre-Lab**

Substance	Formula	Structural Formulas	Molecular Weight	Hydrogen Bond (Yes or No)
ethanol	C <sub>2</sub> H <sub>5</sub> OH			
1-propanol	C <sub>3</sub> H <sub>7</sub> OH			
1-butanol	C <sub>4</sub> H <sub>9</sub> OH			
n-pentane	C <sub>5</sub> H <sub>12</sub>			
methanol	CH <sub>3</sub> OH			
n-hexane	C <sub>6</sub> H <sub>14</sub>			

**Data Table**

Substance	t <sub>1</sub> (°C)	t <sub>2</sub> (°C)	Δt (t <sub>1</sub> -t <sub>2</sub> ) (°C)	Predicted Δt (°C)	Explanation
ethanol					
1-propanol					
1-butanol					
n-pentane					
methanol					
n-hexane					



## References

- Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, 4th ed. Hoboken, NJ: Wiley, 2003.
- Brown, Theodore E., H. Eugene LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*. 10th ed. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.
- Whitten, Kenneth W., Raymond E. Davis, M. Larry Peck, and George G. Stanley. *Chemistry*. 8th ed. Belmont, CA: Thomson/Brooks/Cole, 2007.
- Zumdahl, Steven S., and Susan A. Zumdahl. *Chemistry*. 7th ed. Boston: Houghton Mifflin, 2007.

## Sources for Graphics

- Dipole-dipole attraction (Image #45): Brown, Theodore E., H. Eugene LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*, p. 446. 10th ed. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.
- Dipole-dipole attraction and hydrogen bonding (Images #46 & 47): Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, p. 507. 4th ed. Hoboken, NJ; Wiley, 2003.
- Hydrogen bonding (Image # 48): Brown, Theodore E., H. Eugene LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*, p. 451. 10th ed. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.
- Boiling point vs. molar mass (Image #49): Kenneth W. Whitten, Raymond E. Davis, and M. Larry Peck. *Chemistry*, p. 490. 6th ed. Belmont, CA: Thomson/Brooks/Cole, 2007.

## VII. Further Bonding Issues — Beyond AP<sup>®</sup>

Arden P. Zipp

Despite the success of Lewis dots, VSEPR and the valence bond (VB) theory in dealing with a wide range of chemical species, there are several that cannot be treated adequately by these methods. In many of these cases, however, the molecular orbital (MO) theory, which was once included in the AP Chemistry curriculum, can provide answers. An outline of MO theory will be presented to enable the reader to appreciate some applications, if not the details, of this theory. This treatment will be initiated with a consideration of homonuclear diatomic molecules from the second period of the periodic table.

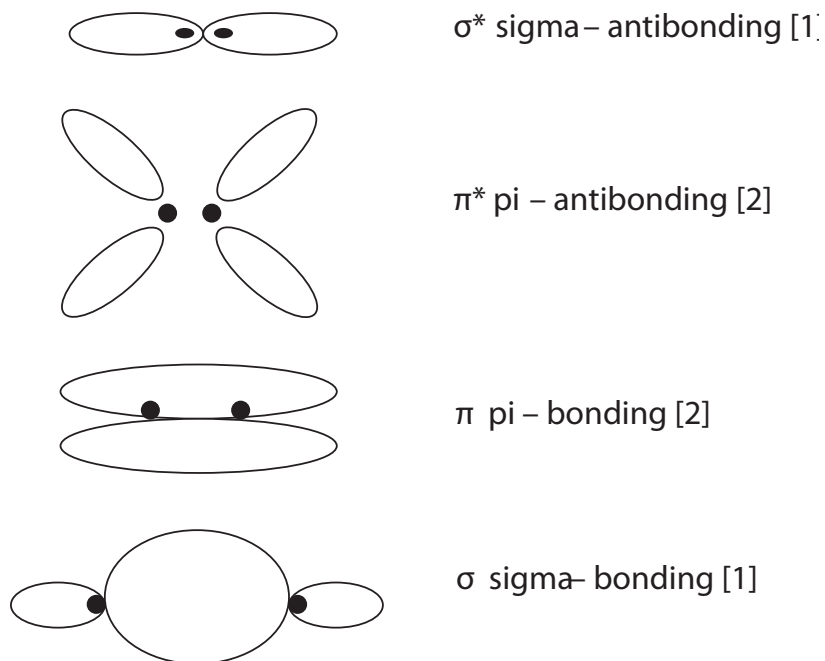
### Molecular Orbital Theory<sup>4</sup>

In this approach to bonding, the bare nuclei of the atoms in a molecule are considered to be embedded in a series of orbitals of specific shapes and energies. Sigma ( $\sigma$ ) orbitals have electron density along the internuclear axes between the atoms while pi ( $\pi$ ) orbitals have electron clouds above and below those axes. Sigma orbitals can be formed from either s or p orbitals; pi orbitals (because of their geometry) cannot be formed by s orbitals but can be formed by p or d orbitals (the latter of which will not be discussed further in this publication). All orbitals may be combined to increase electron density between the nuclei (called a *bonding* orbital) or decrease it (referred to as *antibonding* and designated by an  $*$ ) relative to the separated atoms. The combination of two s orbitals or two p orbitals produce one  $\sigma$  and one  $\sigma^*$  orbital but the two p orbitals yield two  $\pi$  and two  $\pi^*$  orbitals.

If the internuclear axis is assumed to be the z axis, the  $p_z$  orbitals on two atoms can be combined to form one  $\sigma$  and one  $\sigma^*$  orbital. The  $p_x$  orbitals on these two atoms can form one  $\pi$  and one  $\pi^*$  as can the  $p_y$  orbitals on the same two atoms, to give two sets of  $\pi$  and  $\pi^*$  orbitals. The MOs formed by the p orbitals in a typical period from (highest to lowest energy) are shown below. (In each diagram the nuclei are represented by dots.)

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4. Brown, Theodore E., H. Eugene LeMay, and Bruce E. Bursten, *Chemistry: The Central Science*, 5th ed. (Upper Saddle River, NJ: Prentice Hall, 1990), 318.



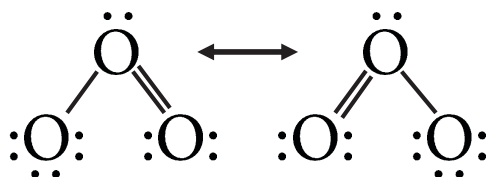
Electrons are added to these orbitals in order of increasing energy, with a maximum of two electrons per orbital (in the same manner that electrons are added to atomic orbitals in individual atoms). Electrons added to bonding orbitals increase the stability of a species, while electrons in antibonding orbitals destabilize a species. The MO theory contrasts with the VB theory in which s and p (or hybrid) orbitals retain their shapes as they overlap to form bonds.

One of the earliest successes of the MO theory was a description of the bonding in the oxygen molecule,  $O_2$ . Although the double bond in  $O_2$  can be predicted with a suitable Lewis structure and represented by means of the valence bond theory, both of these approaches fail to predict that  $O_2$  in its ground state is paramagnetic, possessing two unpaired electrons. However, these results are given by the MO theory, which places one electron in each of the two  $\pi^*$  orbitals, making the molecule paramagnetic while also giving it a bond order of two due to an excess of four more bonding electrons than antibonding ones. A new technique, photoelectron spectroscopy (PES), which can provide information about the energies of electrons within molecules, supports these results.<sup>5</sup>

A second aspect of bonding that is explained better by the MO theory than by either the Lewis or the VB theory is the bonding in species with delocalized electrons. The Lewis theory treats this phenomenon by constructing two or more equivalent structures (called *resonance forms*). The real structure is considered to be intermediate between these different forms but cannot be represented within the constraints of the Lewis theory.

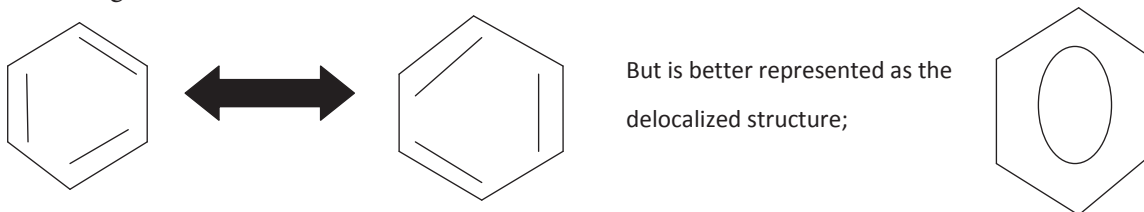
5. Miessler, Gary L., and Donald A. Tarr, *Inorganic Chemistry*, 3d ed. (Upper Saddle River, NJ: Pearson/Prentice-Hall, 2004), 131.

As an example, the structure of ozone is represented as:



In contrast, the MO theory treats the molecule as a whole with the three bonds (two  $\sigma$  and one  $\pi$ ) distributed across the two bonding regions that connect the three oxygen atoms. Thus, each pair of atoms is held together by one  $\sigma$  and one-half of a  $\pi$  bond, resulting in a bond that is intermediate in strength between a single bond and double bond. (This is the same result as that obtained by averaging the strengths of the single and double bonds predicted by the resonance forms with the Lewis theory but without the artificial nature of that approach.)

A similar treatment applies to benzene,  $C_6H_6$ , which can be represented by the following resonance forms:



**Problem:**

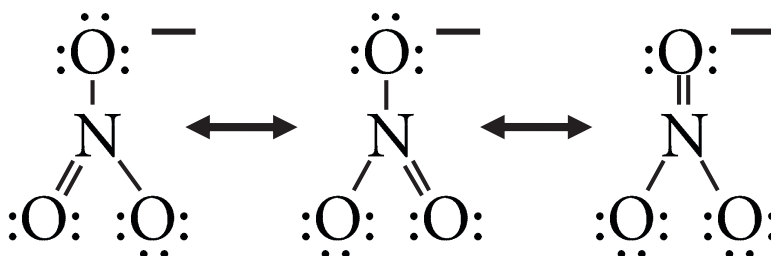
The nitrate ion,  $NO_3^-$ , has a trigonal planar geometry with N in the center.

- Determine the number of valence electrons in this ion.
- Write the possible resonance forms.
- Predict the geometry of the  $NO_3^-$  ion and outline your reasoning.
- Determine the average bond order in the delocalized representation of this ion.
- Describe how MO theory would treat this molecule.

**Solution:**

(a)  $N$  (5 val.  $e^-$ ) + 3  $O$  (6 val  $e^-$ ) + 1 $e^-$  = 24 valence electrons

(b)



- The  $NO_3^-$  ion will be trigonal planar. The central atom (N) is surrounded by three charge centers.
- The N-O bonds would each have bond orders of  $1\frac{1}{3}$ .

- (e) The MO theory would consider the four bonds (three  $\sigma$  and one  $\pi$ ) to be distributed across the three bonding regions, giving a net bond order of  $1\frac{1}{3}$ .

## Hybridization Revisited

Hybridization (as developed within the valence bond theory) is a very useful tool for accounting for the geometries of many species. However, recent PES results disagree with some hybridization predictions. Specifically, the valence bond theory pictures the carbon atom in methane as  $sp^3$  hybridized with four equivalent bonds between the carbon and the four hydrogen atoms. Such a structure should produce a PES spectrum with a single line for these four bonding orbitals, whereas it actually shows two lines (in an intensity ratio of 3:1). The simplest explanation based on these results is that the C 2s and 2p orbitals bond individually to the H atoms rather than being transformed into four “hybridized” orbitals with equal energy. (The more intense line in the PES spectrum corresponds to bonds formed between the Hs and the 2p orbitals of the carbon, while the less intense one reflects a bond involving the C 2s orbital.)

Another species that the VB theory represents as hybridized is sulfur hexafluoride,  $SF_6$ . In this case, an s, three p and two d orbitals on the sulfur atom are envisioned as forming six equivalent  $d^2sp^3$  orbitals, which overlap with p orbitals from six fluorine atoms to form this octahedral species. In contrast, the MO theory pictures this molecule with the six fluorine atoms bonded to the sulfur via four bonding and two nonbonding orbitals. The four bonding orbitals are in two sets, a single low energy orbital and a set of three higher energy ones. These bonding orbitals are derived from the s and p orbitals on the sulfur, so the structure of  $SF_6$  can be accounted for without invoking d orbitals at all!<sup>6</sup>

These few examples show that there are aspects of chemical bonding that go beyond those presented in the earlier sections of this Curriculum Module. To reiterate a point made earlier, various bonding theories represent attempts to account for results obtained experimentally. As new experimental techniques, such as PES, are developed and yield new results (such as those obtained for  $CH_4$ ), it may be appropriate to modify or even discard theories that have previously been useful. That is the nature of a dynamic science such as chemistry.

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6. Shriver, Duward, and Peter Atkins, *Inorganic Chemistry*, 4th ed. (New York: Oxford University Press, 2006). 64.

## About the Authors

**Marian DeWane** has served as an AP Question Leader for the AP Chemistry Examination and has also served as an AP Reader and Table Leader. She has served on the American Chemical Society Exams Institute Advanced High School Committee and the National Chemistry Olympiad Task Force.

**Valerie Ferguson** teaches AP Chemistry at Moore High School in Moore, Okla. She has served as an AP Reader and Table Leader for the AP Chemistry Exam. She also works as a consultant for the College Board and is an instructor in the Summer Institutes for AP Chemistry teachers. She has served as chair of the Oklahoma chapter of the American Chemical Society, president of the Oklahoma Science Teachers Association, and was co-organizer of the “Teaching AP Chemistry” symposium at the 14th Biennial Conference on Chemistry Education.

**David Hostage** is the head of the Science Department at the Taft School in Watertown, Conn., where he has taught chemistry and biology since 1984. He has been active in many aspects of the AP Chemistry program, including teaching the course since 1986 and leading workshops since 1988. He has been an AP Reader and Table Leader for the AP Chemistry Exam and served for four years on the AP Chemistry Development Committee. Hostage was the founding content adviser for the AP Chemistry Web page on AP Central® and has been a reviewer of previous AP Chemistry special focus publications. He is the author of an examination review book and a laboratory manual to support AP Chemistry. He has also been a member of the Examinations Task Force that prepares written examinations for the American Chemical Society’s National Chemistry Olympiad Program.

**Adele Mouakad** has taught AP Chemistry since 1983. She has won the Presidential Award for Excellence in Science Teaching and was a member of the Woodrow Wilson Foundation Teacher Outreach Program and a Dreyfus Master Teacher. Mouakad has been an AP Reader for the AP Chemistry Examination and has been a member of the National Chemistry Olympiad Task Force.

**Arden P. Zipp** retired recently from his teaching position at SUNY Cortland, where he taught for 41 years in the Chemistry Department (including 22 years as a Distinguished Teaching Professor). He has been active in the AP Program since 1975 and has participated in 24 AP Chemistry Readings as an AP Reader, Table Leader, Question Leader and Chief Reader; he also chaired the AP Chemistry Development Committee for four years. Zipp is the author or coauthor of more than 40 papers on inorganic chemistry and chemical education. He has delivered more than 240 presentations in workshops and institutes, including 70 for the AP Program. A contributor to the American Chemical Society’s National Chemistry Olympiad Exam since 1986, he has chaired the task force that prepares the written exams for the past 15 years and was recently appointed as chair of the NCO subcommittee. He is also active in the International Baccalaureate Chemistry Program and served as Chemistry Chief Examiner for that organization for several years.

